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A SPECTROPHOTOMETRIC STUDY OF SOLUTIONS OF COPPER AND COBALT.

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I. Introduction and Object of the Investigation.

THE color of substances in solids or in solutions has been the subject of many investigations and its literature is very extensive. Many important features are observed by the unaided eye. Such, for example, are the complementary colors of transmission and reflection, and the change in absorption due to change in thickness. The instruments used in the study of color are also numerous. The methods are colorimetric, photographic and spectrophotometric, or these methods in combination. The latter only gives accurate quantitative measurements of absorption. All methods have features to commend them. The first step beyond the use of the unaided eye is the use of the spectroscope and eye to mark the region of absorption. Bunsen [1] and others early used this method. By means of cross wires the region between light and dark is determined. This method has been extensively used by Ostwald [2] and Hartley [3] who arrived at diametrically opposite conclusions upon the conditions of substances in solution. Both combine the method with the photographic process which leaves a permanent record of the character of absorption. Hartley modifies his observations by resorting to the common method of placing the absorbing solution in a wedge-shaped vessel whose angle is at right angles to the refracting angle of the spectroscope prism. By this means he obtained spectral absorption showing different intensity at top and bottom,

and a sloping curve across limited portions of the spectrum. The slope indicates the sharpness of the absorption. This method is an excellent one to give a comprehensive view of absorption, and, apparently, was so regarded by Ostwald; but it is possible to overestimate its value. Hartley appears to do this. In his criticism of Ostwald's work he emphasizes the importance of a sharp location of the band. Now, it is clear that the absorption bands shade off into the light regions by degrees. There is no discontinuity approaching that of the line spectrum; consequently, a difference in concentration may cause the same darkening as an increase in temperature does in some of Hartley's experiments. So that it is here necessary to use precaution in making fine distinctions. The most important thing, however, in color study is the determination of the absorption throughout the whole spectrum band, and nominally transparent region, for upon the intensity of absorption, as well as the position, the color depends. The spectrophotometric method involves a quantitative matching of two beams of light, one of which is reduced in intensity by passage through the absorbent. The instruments used for this work are also numerous, but those using the principle of a vanishing line when intensities are equal are superior to those which require the observer to judge equal illumination. With the eye the spectral limits of observation are limited, only the central region of the spectrum can be observed. The photographic record can be taken much farther in the short waves. A combination of photographic and spectrophotometric is here possible. The rays of different intensities have varying degrees of action upon photographic plates, and these plates may afterwards be examined for absorption when there may be obtained quantitative results of a high order of accuracy.[4] The thermopile, or, better, the bolometer, or the radiometer, is also a commendable method for quantitative study. These are particularly applicable for waves longer than the eye can measure.[5] These methods of study may be used for various purposes. A pure product may have a certain color or absorption and the same product in an impure or inferior form quite different absorption. The method may be used to study the law of absorption. Beer's law requires that the ratio of transmitted light shall be equal to $e - kcl$, where c is the concentration, l the thickness and k

a constant, sometimes designated as the extinction coefficient, depending upon the wave-length and nature of the absorbent. The reasons for the Beer's law are apparent and its confirmation in such substances as colored glasses or solutions where thickness only varied, was an easy matter, but the early literature shows no such agreement when the concentration of solution varied. Some confirmed the law; others did not do so. There were two reasons for non-confirmation: Firstly, some of the methods of measurement were not sufficiently refined; and, secondly, and more important, there were changes in the character of the solutions when concentration changes occurred. When the theory of solution developed so that this fact was recognized, Beer's law became an important so that this fact was recognized, Beer's law no longer became the point of strife, but the changes in color, and, consequently changes in the coefficient in Beer's law became an important index of the changes of solution, *i. e.*, color methods of study became an important method of studying the physical and chemical properties of solutions, *e. g.*, the change from the molecular to the ionic condition in dilute solutions. Ostwald[2] clearly outlined this phenomenon when he enunciated the law that substances which contain a common colored ion have a given color in dilute solution.

The outline in the present experiment was to follow some of the color changes by the spectrophotometric method. This method requires, generally, observations at several points in the spectrum. It is, therefore, somewhat tedious and irksome in comparison with other spectral methods, or even in comparison to kindred methods of approaching the same question; *e. g.*, the freezing-point method, or electrolytic conductivity methods. The work is as many times greater as there are points studied in the spectrum. To this must be added repeated observations to be sure of accuracy. Color changes are sometimes apparent enough, but of small magnitude. Under such circumstances the most that can be obtained from quantitative measurements is qualitative results. Results in spectrophotometry have, generally, been of this type; *i. e.*, they were indicative only of general processes in solution. That is, quantitative calculations can not be made from quantitative readings like it is possible to do in electrolytic measurements or freezing-point de-

terminations. A recent attempt by Vaillant[6] to make results quantitative have been attended by considerable success. He gives errors in results as large as 10 per cent. This does not mean errors of that magnitude in the spectrophotometric measurements, but errors arising from an application of the exponential formula. The present author followed quantitatively the hydrolysis of ferric chloride[7] by means of the spectrophotometer. The exponential formula was necessary here also. This led the author to the conviction that spectrophotometric observations need several times their present accuracy before thoroughly reliable quantitative calculations can be made. But, withal, the method is a great advance over the method of mapping absorption fields. A number of observers have followed the changes upon diluting water solutions, spectrophotometrically, and have generally confirmed the dissociation hypothesis. Vaillant[6] alone seems to have made a thorough quantitative comparison of dissociation, obtained from electrical data, with the absorption. In general he found a close parallelism between the observed and the computed absorption. There were marked differences in some concentrated solutions, which suggest the presence of other products. These he calls hydrates, but in the course of this paper it appears that these may be other products. The work upon permanganates may be mentioned here, inasmuch as Hartley[3] dissents from the conclusions drawn by Ostwald[2] upon these solutions. Hartley retains the conception of the complete integrity of the molecule — an opinion which he confesses to have formed before the theory of ionic dissociation was developed; and, farther, maintains that salts containining water of crystallization still contain this water in solution as an integral part of the molecule. Then he adds to this the physical theory of absorption,[8] *viz.*, that absorption arises from molecules whose periods of vibration are the same as the light which they absorb; and draws the conclusion that molecules vibrate as a whole or as units, showing an absorption which depends upon the period of vibration. A change in weight of the molecule must change the period and there must be some shift of the absorption bands. In the permanganates Ostwald marks the position of four bands (instead of one band, as Hartley reports), and all retain, practically, the same position for all salts in

dilute solutions. Hartley contends for a greater dispersion when there is so little difference in the weight of the salts in the electropositive series as in these permanganates. Such a process means, in general, a lack of definition.

Pflüger,[11] Vaillant[6] and the present writer[12] studied these salts spectrophotometrically. Pflüger's work covered eleven salts of great dilution at one point in the spectrum, *viz.*: at 576 $\mu\mu$, and at the same point in the spectrum he also studied solutions of Na^-, K^-, and Ba^- permanganates of 1,000 times as concentrated as the dilute solutions. Taking into consideration the degree of dissociation the latter three all show the same absorption coefficients. Vaillant studies K^-, Ba^-, and Zn^- permanganates at four different points in the strong absorption region. These were studied at several concentrations, but mostly of great dilution. From the electrical conductivity of all, and the absorption of one the absorption of the other solutions may be calculated. The absorption so calculated agrees well with the observed values, and hence the conclusion that the absorption depends upon the ionization. The data for the more concentrated solutions show values of absorption for the molecules slightly different from the ions and also slightly different from each other. It was possible for the molecules to have all absorbed alike. Vaillant contends that the variations could just as well arise from variation in the state of hydration of the molecules as from the ionization. The general agreement with the ionic theory observed by these experimenters, does not answer the objection of Hartley. The present writer followed the absorption throughout the entire spectrum, taking readings about every 10 $\mu\mu$ in the principal absorption regions, and in the region between the principal absorption and the nominally transparent portion of the spectrum. The readings were limited to two salts K^- and Zn^- permanganates in concentrated and in dilute forms. Although very limited in the number of salts studied, the spectral study was very complete and could answer Hartley's contention so far as these salts were concerned. The experiments suggested the Ostwald theory but were not conclusive. In the bands the zinc concentrated and dilute and the potassium dilute were practically identical. The potassium concentrated alone differed, and this was a small differ-

ence in intensity but not in position. The concentrated zinc was about one fourth the concentration of the potassium. In the nominally transparent region the dilute solutions absorbed more than the concentrated, and were nearer equal to each other than to the concentrated, and also nearer than the concentrated were to each other. The identity of the solutions throughout the spectrum seemed to be possible, but it was not a necessary conclusion. Yet, there was a certainty of identity in position of the absorption bands, for which Hartley[3] contends.

The law of mass action requires that the introduction of an ion into a solution containing an identical ion, will repress the latter to a greater or less extent into the molecular condition. When such an ion is colored, this action, if present, may be followed spectrophotometrically. It occurred to the writer that substances in dilute solution could thus be forced to return to their form, and, therefore, to the absorption, in concentrated solutions; and possibly to obtain, even, solutions with less ions than the original concentrated solution. With this hypothesis the writer mapped out a study of the salts of cobalt, copper and nickel. As then outlined these salts were to be studied in concentrated and dilute water solutions and with acids having an ion in common with the negative ion of these salts. This treatment of the copper and cobalt salts was reported to the St. Louis meeting of the Physicial Society in September, 1904. It was then suspicioned that certain irregularities could be explained by variation in the concentration of the acids and the presence of hydrates in solutions as outlined by Jones and colaborers. Hence the scope of the work was broadened to treatment of diluted solutions in acids of varying concentrations and in salts containing the same negative ion as the dilute solution.

In the past year the pressure of other work has only permitted the application of this principle to cobalt sulphate and cobalt chloride. The other results are the same as reported at St. Louis, except that they have all been repeated. The results already obtained indicate the desirability of applying the method to the substances originally contemplated, but unforseen events in the department of Physics make it impossible to take up the work before, at least, another year; so that, rather than delay for completion, the present

work is sent to the press. If the present results indicate possibilities or stimulate further inquiry, the work will have some value.

The plan of mixtures and a change in the solvent has been followed by Vaillant[6] in a very comprehensive spectrophotometric investigation. Many of the substances and mixtures herein studied were also studied by Vaillant. He studied more solutions and computes absorption coefficients from a comparison with the electrical data. His observations were limited to a few points in the spectrum, generally three within the band and close together, but sometimes as many as six points. The writer has studied many less solutions, but has observed throughout the spectrum, trying to make the spectrophotometric observations complete. So that, what one observer has done the other has left undone. The solutions are different in all respects except in name. The treatment is generally different. The discussion is radically different. The present writer had in mind during the progress of the experiments some investigations made about the time of Vaillant's publication and subsequent thereto.

II. Experimental Method.

The Brace Spectrophotometer[14] was used throughout the experiments, and the method of using and adjusting it was the same as in other contributions. Therefore the following brief description will suffice. In Fig. 1, the light from the opposite sides of a small isolated section of a flat acetylene flame passes on the left through a tube T_1, lens L_1, reflected from mirror M_1, focussed upon slit S_1, thence through the collimator to prism P, and lastly to the observing eye at the telescope O. The light upon the side passes through a similar path, but within the prism is reflected from a silver strip and thence through the telescope O. The two fields are adjacent, with a line which vanishes when the fields are matched in intensity. The slit S_2, was fixed at about .8 mm. in width. The slit S_1 was variable and read with the telescope O'. Generally the absorbent was placed in the position T_2 and no tube placed in the

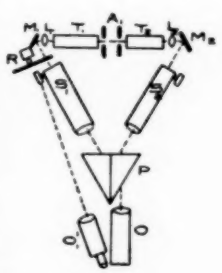

Fig. 1.

position T_1. T_1 was generally filled with the same product as T_2 except that the colored component was omitted. This tube was then placed in the position T_2 and the slit S_1 adjusted for a match at the point of the spectrum wished. Tube T_1 is next replaced with tube T_2 and a new setting of the slit made.

To avoid large changes in S_1 and, consequently, the calibration of the slit, a rotating sector was used in connection with the slit. The latter was always adjusted so that the slit S_1 need be closed only a small per cent. The ratio of the intensity of the beams transmitted by the tubes T_2 and T_1 is thus measured. This is readily seen to be the per cent. of light transmitted by the colored component only, without any corrections whatsoever. For very transparent portions of the spectrum the first setting of the slit S_1 is made with tube T_2 in position T_1, and T_1 in position T_2 and a small absorbent placed before S_2 so as to avoid opening S_1 beyond its normal width. The tubes are then interchanged and another setting made. These tubes were made in pairs; the shortest pair was each 10 mm. long; the longest pair 300 mm. long. Reversing the position gave length up to 600 mm. Concentrated solution in strong absorption region was studied in wedge-shaped vessels. These were usually about .1 mm. (platinum) on one end, and about .85 mm. (tinned pins) on the other end. The transmission walls were of plate glass, uniformly clear, and about 10 mm. thick. A glass plate bottom was sealed on the outside with laboratory cement. By observing through two different thicknesses the absorption arising from increased thickness is obtained. This thickness is determined from the slope and the horizontal displacement. The end plates of the tubes were fastened by paraffin to the tubes on the outside, which while still warm is drawn by capillarity between the ground end of the tube and the plate. The plates are then held by clamps. These end plates were selected with regard to their optical uniformity, but to keep them optically clean proved about the most tedious part of these experiments. In the study of cobalt sulphate, mixed with sulphuric acid, but one tube was used. Readings were taken throughout the entire spectrum with acid and then with the tube filled with cobalt and acid mixture. This required less care and generally expedited matters, but sacrifices some

in accuracy. Generally five readings were taken for the first setting of the slit, ten for the second setting, and again five for the first.

Color measurements were made at the temperature of the room, which varied from 20° C. to 25° C., but usually from 23° C. to 25° C. This temperature change could be of little importance unless in cobalt chloride. The acid solutions of this salt were studied in very warm weather, when the temperature ranged from 25° C. to 27° C. All chemicals used in these experiments were purchased from the Mallinckrodt Chemical Works of St. Louis, and marked chemically pure. The crystals of the copper salts were washed and then dissolved in warm double distilled water and allowed to precipitate by cooling. From the crystals so obtained the solutions were made. After long standing, new stock solutions were required. Cobalt solutions were made from the purchased samples. To determine densities a calibrated Mohr's balance was considered sufficiently accurate. The water used in all cases was double distilled. The per cent. of salts in solution was obtained, when possible, from Landolt's & Bernstein's Tables; in other cases it was necessary to make a quantitative chemical analysis of the solution. From per cent., densities and molecular weight values (oxygen equal to 16 in these tables), the equivalent concentration is computed. The solutions were diluted by means of an accurately calibrated pipette (5 c.c.) and flasks with small necks.

Beer's law is used to reduce the observations through different lengths and in various concentrations to a common basis. Using A as the reciprocal of K in Beer's law, we have

$$A = \frac{cl}{\log \frac{l_0}{i}}$$

where i is transmitted light and l_0 the incident light, C the equivalent concentration, and l the length expressed in millimeters. A is that thickness in millimeters of a solution of one equivalent which transmits 10 per cent. of the incident light. This may be called the equivalent transmission coefficient. I have generally used this term instead of its reciprocal, K, designated the equivalent extinction coefficient. Although many data are published in terms of K, I have

made the change because the term extinction coefficient is frequently used in optics with another meaning. Further, the thickness required to cut out a certain portion of the light is just as comprehensive, if not more so.

In the tables, the first row gives the concentration of the salt under study; the second row gives the concentration of the acid or transparent salt used. Zero acid means a water solution. The wave-lengths in $\mu\mu$ are recorded in the first column; the values of A in the other columns. The latter correspond to the concentrations under which they are placed.

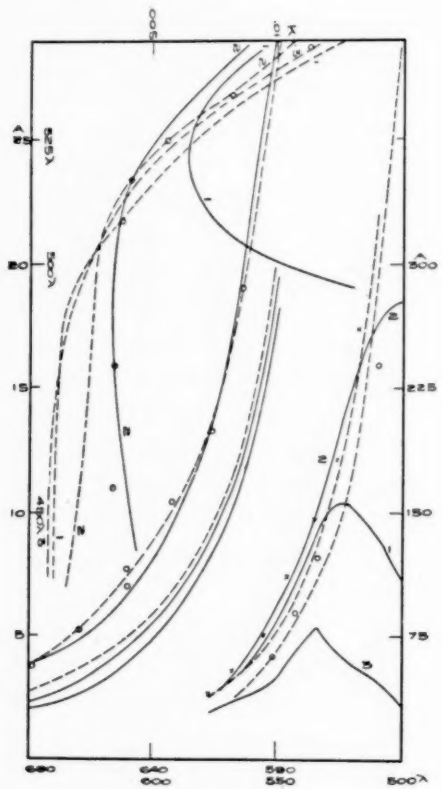

Fig. 2.

Fig. 2 gives a graphical presentation of the copper solutions. The continuous lines refer to the copper chloride solutions; the

broken lines to the copper nitrates. The small "x's" and circle "o's" refer to the readings for the concentrated and dilute copper sulphates respectively. These substances are shown on three different scales on account of great changes. In the blue the reciprocal of A, *viz.*, the equivalent extinction coefficient is plotted.

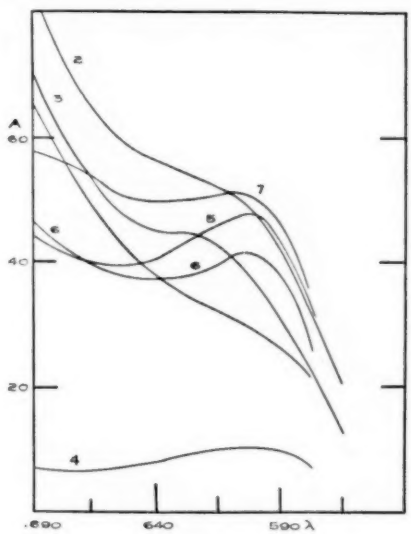

Fig. 3.

Fig. 3 gives the red end of the spectrum for water solutions of all the cobalts. The numbers have the following significance, *viz:*

1, ½ $Co(NO_3)_2$ = 5.45	2, ½ $Co(NO_3)_2$ = .0545
3, ½ $Co(NO_3)_2$ = .0545 + acid	4, ½ $CoCl_2$ = 6.8
5, ½ $CoCl_2$ = .034	6, ½ $CoSO_4$ = 4.85
	7, ½ $CoSO_4$ = .0485

Fig. 4 refers to the blue end of the spectrum of dilute solutions of cobalt in water. The curve shows the cobalt nitrate; the crosses "x" and the rings "o" show the cobalt sulphate and cobalt chloride respectively. Figures 5 and 6 give the red and blue spectra respectively of the cobalt chloride solutions. Figures 7 and 8 are the red and blue spectra respectively of the cobalt sulphates. The numbers on the curves, in all cases, refer to the columns in the corresponding tables. For example, in Figs. 7 and 8, take the number 8; it is a

curve for the column of data under eighth *A* of Table VIII. of cobalt sulphates. Where the concentration $\frac{1}{2}(CO - SO_4)$ is .0243 and the concentration of $\frac{1}{2}H_2SO_4$ is equal to 21.3. In all tables the obser-

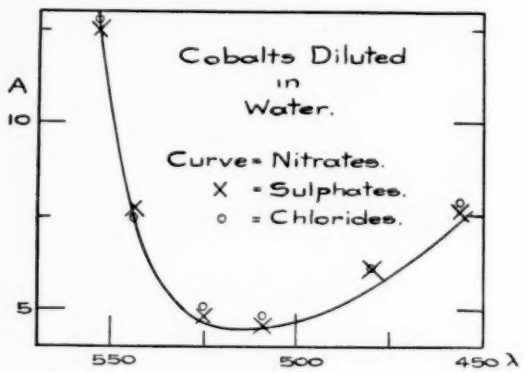

Fig. 4.

vations in parenthesis correspond to one set of readings only. The other results are the mean of three determinations. In the treatment of cobalt, chloride and sulphate, with strong acids, the mean is for different concentrations of cobalt and constant strength of acids.

TABLE I.

$\frac{1}{2}CuSO_4$.

$\frac{1}{2}CuSO_4$ $\frac{1}{2}H_2SO_4$ λ	2.86 o *A*	2.693 o *A*	2.63 o *A*	2.596 o *A*
690.0	4.24	4.32	3.90	4.10
669.0	5.46	5.56	5.38	5.45
650.0	7.27	7.48	7.36	7.20
632.5	10.1	10.6	10.8	10.1
616.5	14.6	13.5	13.8	14.5
602.5	20.1	21.0	21.1	20.0
589.6	28.5	26.4	30.3	28.3

The solutions in Table I. are all freshly prepared, *i. e.*, no more than a few days old and made by methods previously described. They were also made on widely different dates. Their mean value is incorporated in Table II. under concentration 2.63. Their variation represents the degree of accuracy obtainable. The rest of

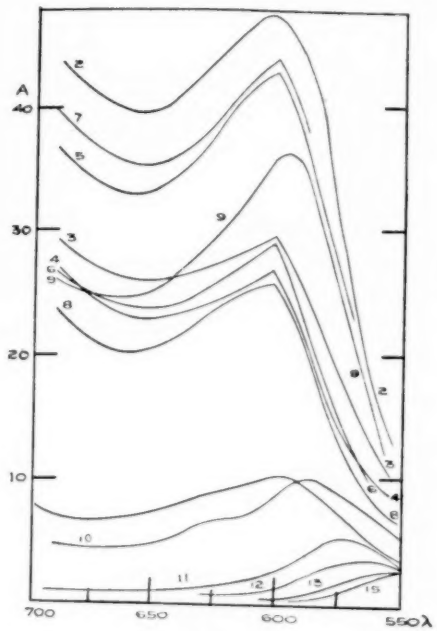

Fig. 5. $CoCl_2$.

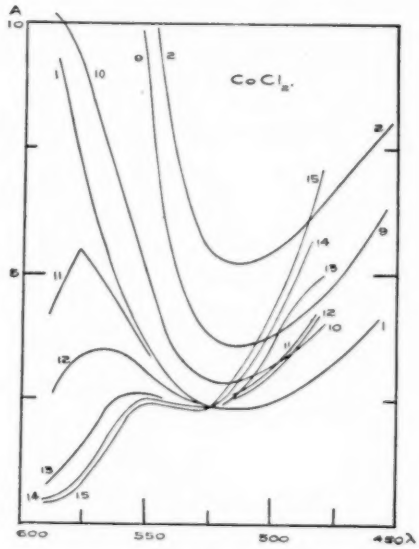

Fig. 6.

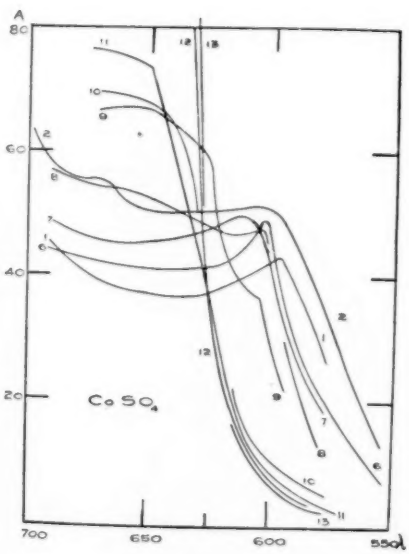

Fig. 7.

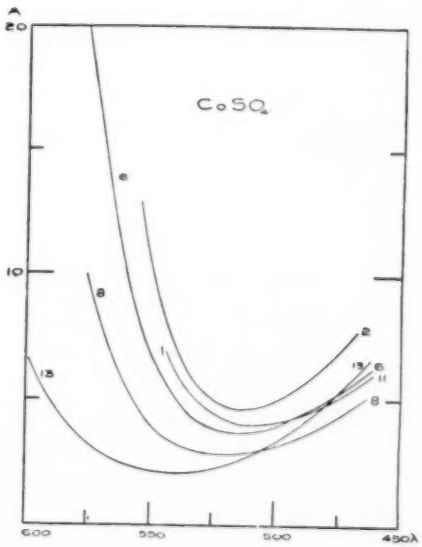

Fig. 8.

Table II. corresponds exactly to the concentrations there given. The results are the mean of three different sets of readings. It was necessary to use liquid columns of three different lengths in the different parts of the spectrum. Consequently, the spectrum could not be completed in one period of observation. When the dilute solutions stood for a day or longer there seemed to be changes, but these had no uniformity in their nature. Sometimes the solution would become more transparent, and at other times more opaque. This was particularly noticeable in the copper nitrates. The author therefore decided not to trust old solutions, but to make up fresh diluted solutions to finish uncompleted observations. In the last two columns of Table II. alone there were twelve such solutions prepared.

TABLE II.

$\frac{1}{2}CuSO_4$.

$\frac{1}{2}CuSO_4$ $\frac{1}{2}H_2SO_4$ Å	2.63 o A	.0526 o A	.0526 5.08 A	1.232 o
690.0	4.14	3.97	4.23	
669.0	5.46	5.35	5.41	
650.0	7.33	7.65	7.52	7.4
632.5	10.4	10.45	11.6	10.6
616.5	14.1	14.3	15.6	14.9
502.5	20.6	19.1	24.0	21.3
589.6	28.4	28.7	35.6	31.2
577.0	40.7	40.6	40.6	43.5
564.5	57.2	53.0	—	69
553.5	78	63.2	63.2	100
543.5	111.4	88.6	91.2	125
534.0	150.6	122.4	175.2	182
525.0	190.6	182	285.3	263
517.0	265.8	248.9	—	400
509.0	283.4	268.9	—	555
494.0	—	—	415	
479.5	293	286.9	—	2000
468.0	—	—	443	
456.0	319	288.2		
436.0	—	251.8		

Grünbaum [15] states that it is necessary to filter repeatedly in order to remove dust from the solutions. The author has not found nor heard of a process of filtering that will make solutions optically

clear. Spring states that a colloid hydrate will do so. However, a sample of copper sulphate taken from the stock which has stood a day generally shows less diffusion in strong light than a repeatedly filtered one. Distilled water will also show diffusion. A satisfactory solution is the reduction of this diffusion to a minimum in the absorption and comparison tubes and then assume it to be the same in the two tubes. Copper nitrate in dilute solutions certainly decomposes and the behavior of dilute copper sulphate solutions on standing suggested the same phenomena. Hence the author's distrust of old diluted solutions. Sometimes in the transparent region it was easy to get variable readings with solutions as prepared when first added to the absorption tubes, but after half an hour standing the readings were constant. Readings were seldom taken before an hour, and solutions always stood twice that long before a set of readings could be completed.

In Table II., last column, is given data interpolated from the curve of Grünbaum's data [15] and reduced to the same basis as the author's readings. His readings were selected rather than those of Müller [16] or Ewan [17] because they extend much farther into the absorption bands. Copper sulphate is selected because concentration changes make no important difference. These readings agree well, where absorption is large, but in the regions of great transparency differ enormously. Grünbaum's hypothesis, before-mentioned, of dust in suspension is not tenable, for upon dilution the discrepancy is greater, whereas the water tube should contain a trifle more diffusion than the other, and hence an action towards increasing the apparent transparency. Müller's limited data agree well with those of Grünbaum's and both differ from Ewan by 40 per cent. in this region. The author cannot attribute the remarkable variation to difference between old and new diluted solutions, inasmuch as he knows nothing about the experience in this respect of Messrs. Ewan, Grünbaum and Müller. Neither did he make a study of old solutions for apparent reasons. If he even conceded an error in his absolute values the phenomena has evidently entered the sulphate, chloride and nitrate of copper in an identical way, and in no wise affects the results for comparison and conclusion.

In the concentrated sulphuric acid solutions, and slightly in the nitric acid solution, there was trouble due to minute air bubbles in suspension which caused dispersion in the transmitted light. These get into solutions in mixing and in decanting into the transmission tubes. It was found best to allow these tubes to stand about two hours before taking observations. Many air bubbles then collect at the top of the tube where they do not effect the transmitted beam. In some cases all bubbles are not gone in a day's standing, but generally after two hours it was assumed that the two tubes were near enough in the same condition to warrant observations. Four hours would give the same results, whereas a day's standing might show either turbidity or a precipitate, and, at least, irregularities.

III. THE COPPER SOLUTIONS.

The copper salts all have a common absorption band in the red (Fig. 2), which would give them in solution a dark blue color. Copper chloride, in a strong solution, absorbs also in the blue, which leaves this solution green. According to the Ostwald theory,[2] we may then look for ionic absorption in the common band. This result is exceptionally well verified in the red absorption region, where upon dilution the absorption in the nitrate, sulphate and chloride are practically identical both in position and magnitude. But it is also clear that this absorption region is not due to the ions alone in the solution in general; for then the region would grow relatively darker upon dilution. The opposite effect takes place in the nitrate and chloride. There is no change in the sulphate. This indicates that in whatever region there is ionic absorption there is also molecular absorption, and it is clear that the molecular absorption is greater than the ionic in the nitrate and chloride, and equal to it in copper sulphate salt. The chloride and nitrate molecule absorb more than the copper sulphate molecule. In the dilutions here studied dissociation is far from complete; so that some difference in the absorption region is expected, even in dilute solution. Since there is considerable difference in the molecular absorption, more difference should have been expected in solutions of the present dilution than was observed. This appears, however, within the limits of error. The action of the acid is ap-

parent. For the chloride and nitrate it has more than restored the dilute solutions to their original condition; *i. e.*, it has repressed the ions to the molecular condition, and shows that relatively there are more molecules in solution than in the concentrated form. The acid makes no difference in the copper sulphate ion; that is, there seems to be no essential difference between the ion and the molecule of this salt.

TABLE III.

$\frac{1}{2}Cu(NO_3)_2$.

$\frac{1}{2}Cu(NO_3)_2$	6.209	2.576	.0787	.0787
HNO_3	7.169	2.804	0	13.72
λ	0	0		
	A	*A*		
690.0	2.67	3.67	3.70	2.37
669.0	3.63	4.54	5.59	3.73
650.0	5.12	6.34	7.07	4.92
632.5	6.78	8.40	9.52	6.83
616.5	9.11	11.9	13.46	10.48
602.5	14.1	16.9	19.2	14.4
589.6	21.8	28.3	27.6	21.6
577.0	—		38.4	31.35
564.5	40.1		53.6	43.56
553.5	—		69.5	61.3
543.5	80.9		94	84.5
534.0	—		135	120.5
525.0	150.5		180	168.6
517.0	—		247	232.4
509.0	316.4		330	307.6
501.5			371	360.4
494.0	597		—	490
479.5	818.5		392	728
468.0	—		—	—
456.0	913		450	993
446.0	—		—	—
436.0	913		666	1201

Were we to regard the results with acid in the nitrate and chloride as a condition of approximately no ions, and from the electrical data estimate the degree of dissociation in dilute solutions, or even assuming the value here found for copper, compute the ionic absorption, we have a means at hand for calculation of the absorption for different concentrations, or for the calculation of the degree of dissociation of various concentrations. When, as before mentioned,

the required accuracy in optical measurements is obtainable, this quantitative method will be justifiable. The present data do not reach this limit of sensibility, but the results show the possibility of the application. Dissolving the substance in an organic solvent, where the dissociation is minute, and calculating the molecular absorption from it and applying these values to water solutions, is a questionable process. This method rests upon the assumption that a substance, so long as its chemical nature is unchanged, has the same absorption in different solvents. This is contrary to Kundt's law,[5] which has generally been confirmed by various experimenters. Vaillant[6] does get almost identical values for the absorption of copper sulphate in alcohol and glycerine at three points (very close together) in the spectrum. This is too fragile a basis to conclude that it has the same color in all organic solvents, or that concentrated water solutions tend toward the limit of organic solutions, or that the undissociated molecules in water have the same absorption as in organic solutions. Ley[24] points out that copper chloride in alcohol is a pure green, in aceton a yellow green, in urethan yellow, in pyridin blue. In all of these the dissociation is small.

When we consider the part of the spectrum where the absorption is small (see Fig. 2) the data are not so readily interpreted. The dilute solution curve of the nitrate differs considerably from the sulphate and chloride. The sulphate and nitrate are much more transparent when acid is added. The same treatment causes the chloride to darken. The nitrate is the most transparent and its curve crosses the sulphate. The concentrated chloride is nearly black in this region, but upon dilution reaches a value almost identical with the sulphate. In the nitrate the action is the opposite and darkens upon dilution. The sulphate again shows no appreciable change upon dilution. The incomplete dissociation of the nitrate molecule is a reasonable explanation of the difference between its dilute solution curve and the one for the sulphate. On the other hand, the dark chloride is as transparent as the sulphate and it must have still considerable quantity of the undissociated molecules present. As seen later in this paper, there is a possibility of attributing this entire dark band to another product in solution, which disappears upon dilution; so that the real copper chloride molecule

may be as transparent as the sulphate, and the absorption upon dilution could be as observed. In great dilution the absorption of the nitrate, sulphate and chloride are probably also identical in this region. This gives complete identity throughout the spectrum.

TABLE IV.

$\frac{1}{2}(CuCl_2)$.

$\frac{1}{2}(CuCl_2)$ HCl λ	6.8g o *A*	.068g o *A*	.068g 4.5 *A*
690.0	2.15	3.92	2.02
669.0	3.47	4.67	2.63
650.0	4.51	6.91	3.96
632.5	6.45	9.73	5.54
616.5	9.11	13.6	8.63
602.5	12.65	20.7	11.7
589.6	19.67	29.1	18.2
577.6	—	36.7	29.1
564.5	52.5	60.9	37.5
553.8	—	—	46.3
543.5	106.5	115.2	64.4
534.0		—	79.9
525.0	156.	180.1	61.6
517.0		—	55.2
509.0	133.7	270.2	45.4
501.5			32.5
494.0	68.4		18.8
487.0			12.9
479.5	33.4	287.6	7.5
474.0	22		5.4
468.0	17.1		4.2
456.0	8.8	238.2	
436.0		(221.3)	

The copper acetate forms a series of values not to be compared with the other data. It is much darker than the nitrate and the sulphate. It has necessarily small dissociation which might appear as a reason for finding no difference between the concentrated, dilute and acid solutions in the band region. But the position of the curves suggest widely different values between molecular and ionic absorption, so that a difference should exist. In the more transparent region there is an action similar to that observed in the nitrate and sulphate, *viz.*, a darkening upon dilution and a clearing

upon adding acid. Müller studied copper acetate in molecular concentrations of .111 and .006. He discovered a marked change upon dilution. His values are all radically different from mine, which suggests that the difference lies, possibly, in the presence of other products in my solutions. The copper acetate was a commercial product and in solution may have contained basic acetate. Vaillant's[6] observations cover three points within the band of copper acetate. He observed double transparency upon dilution and a darkening of nearly four fold upon adding acid.

It is well to examine these solutions from the standpoint of Hartley.[3] The copper sulphate $CuSO_4.5H_2O$ and $Cu(NO_3)_2.3H_2O$ have weights of about the same magnitude, and, consequently little difference in the bands. $CuCl_2.2H_2O$ is thirty per cent. lighter. It should, therefore, vibrate more freely. What acually occurs is, the red absorption band retains the same identical position as the other coppers. Instead of being displaced toward the shorter wavelengths it further absorbs more than either of the other two salts. Beside, there is an added band in the blue and violet.

The theory of Jones and collaborators upon hydrates in solution has little in common with the older hydrate theory. We may best quote from a recent paper:[18] "The theory of hydrates in aqueous solutions is to be sharply distinguished from the old hydrate theory of Mendeléeff which having long since been shown to be untenable, has been abandoned. According to the older theory when a substance like calcium chloride is dissolved in water there are formed certain definite compounds with perfectly definite amounts of water." According to the new theory "the compounds formed are at best very unstable and vary in combination all the way from one molecule to a very great number." . . . "Thus the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least thirty molecules and may have all intermediate compositions depending solely upon the concentrations, temperature being, of course, understood to be constant."

The data of Jones show, generally, relatively more hydrates in dilute solution, and if the molecules and ions are intimately enough associated with the water to effect the freezing point as a whole, we

may expect such combinations to show characteristic periodic vibrations, and, therefore, characteristic absorption. For example, in the dilute solutions containing relatively large amount of water, the total weight of the molecule would not change appreciably by changing one of the ions, and in dilute solutions the salts containing a common ion, would have practically identical absorption. However, the concentrated solutions having relatively less water in combination, would vibrate more rapidly and give shorter wave-length absorption. That is, there would be a shift of the band from blue toward the red upon dilution. This may be illustrated by data taken from a recent contribution by Jones and Bassett [18] which appeared about the time of the suspension of the observations. For a copper sulphate solution of a concentration of .1301 gram molecules they find 27.1 molecules of water associated with each copper molecule; and for a concentration of copper sulphate solution of 4.371 gram molecules 11.4 molecules of water associated with each copper molecule. These hypothetical additions of water molecules are associated intimately enough with the copper to reduce the effective water in the solution, and hence give the equivalent of abnormal concentrations in solution and, therefore, abnormal lowering of the freezing point. The entire molecule in dilute solution is about 1.54 times its weight in the concentrated solution without making any assumptions as to the damping action of a viscous medium or as to the shape of the molecule and assuming inertia proportional to the mass, the period of vibration would be about 2.3 times as long. Beginning, therefore, with an absortion band in the spectrum for a concentrated solution, one would then have upon progressive dilution a band shifting toward the red and ultimately passing entirely out of the spectrum. No such phenomenon is observed in these experiments, and, in fact, if it existed at all, would have long ago been a well-known phenomenon to the unaided eye. The actual conditions are probably such as to leave this an exaggerated illustration, but granting this, one still feels compelled to state that there can be no intimacy of association between the hydrate water and the salt without a displacement of the band, and it appears remarkable that the water is still intimately enough associated to effect the freezing point values.

Hence, so far as the absorption spectrum is concerned, the molecules must be vibrating in their own little sea of associated water much the same as the non-hydrates in any water solution. A salt which forms a hydrate when added to a solution containing a colored solute, may also affect the color and remains to be considered.

TABLE V.

$\frac{1}{2}Cu(C_2H_3O_2)_2$.

$\frac{1}{2}Cu(C_2H_3O_2)_2$ $HC_2H_3O_2$ λ	0.684 o A	0.0342 o A	0.0342 x A
690.0	1.46	(1.55)	(1.40)
669.0	1.60	(1.63)	(1.56)
650.0	1.92	(1.95)	(1.90)
632.5	2.50	(2.65)	(2.49)
616.5	3.50	(3.60)	(3.45)
602.5	5.1	(5.33)	(5.15)
589.6	7.6	8.15	7.69
564.5	(16.4)	16.54	15.75
543.5	(32.0)	31.8	30.45
525.0	(53.1)	52.7	50.6
509.0	(80.7)	81.4	86.0
494.0	—	—	
479.5	(104)	97.7	111.2
468.0		—	
456.0	(95)	82.8	116.8
436.0	(74)	62.9	109

Such a hydrate salt practically increases the concentration of the original salt, and if the latter is colored, its character of absorption would be the same as another solution of increased concentration with other proportions of hydrate water and another degree of dissociation. For example, if the new salt required 90 per cent. of the water present for its hydrate, then there remains to the original components 10 per cent. of the water. This involves a change in the dissociation of the latter, corresponding to a change in concentration. Consequently, there is a change in color if there was a change upon dilution. This is also what would follow from the law of mass action in solutions containing common ions. This process does not involve, however, unless present by reason of the above action, any general change in intensity or color, because if, in the above illustration, there only remains to the colored salt one

tenth of the original water, there remains, also, if absorption is an additive property of the components only, but the equivalent of one tenth of the length. The only question then is whether the repression of the ionization is proportional to the dissociation, *i. e.*, to the free ions of the added salts, or whether it is proportional to the equivalent increased concentration arising from the hydrated salt added. The free ions added can advantageously be those formed from a hydrate which has no ions common to the colored ion. Lewis[19] observed such changes of tint with his colorimeter, which suggests changes proportional to the added hydrates. The phenomenon needs a careful comparison of the conductivity, freezing point and spectrophotometric data.

The copper chloride, which possesses two absorption regions, is here studied only in concentrated and in dilute solutions, but Müller has studied the salt in intermediate concentrations. In this salt there is a rapid change in the blue region out of all proportion to the ionization. These changes cannot be attributed to the hydrate, inasmuch as there is, firstly, no displacement of the band. Secondly, in the red absorption region, the changes are uniform and what might be expected in a change from the molecular to the ionic condition. The irregular changes in band should have been present here also, if found in the other band, for two reasons: Firstly, not all the red band can be attributed to the ions; and, secondly, the new hydrates are supposed also to be associated with the ions, and the total weight of a hydrate does not change much, in a change from the molecular to the ionic form. If the new hydrate possesses no characteristic absorption of its own, there is still an equivalent change in concentration which, likewise, affects the entire spectrum. Therefore, even if the red absorption were due to the ions alone there should be important changes throughout the spectrum out of proportion to the rate of ionization, instead of only in the blue absorption. So that the changes in the blue absorption indicate the presence of another product instead of a hydrate. The investigation of Ley[24] suggested to him that the change from blue to green upon heating dilute copper chloride was a change from

$$CuCl_2 \rightleftarrows Cu^{\cdot\cdot} + 2Cl' \text{ to}$$
$$CuCl_2 \rightleftarrows CuCl^{\cdot} + Cl'.$$

Inasmuch as an increase in temperature is similar in its color effect to an increase in concentration, it is possible that the blue absorption of the concentrated solutions arises from the CuCl, which disappears upon dilution. A similar phenomenon will be later noted in cobalt chloride. Vaillant[6] observes changes in some copper solutions, particularly the bromide, which are out of proportion to the absorption coefficients. His principle readings are in the red band, *i. e.*, the ionic band. If these readings were extended to the whole spectrum they might show the same discrepancy throughout, which would be an indication of the new hydrate.

TABLE VI.

$\frac{1}{2}Co(NO_3)_2$.

$\frac{1}{2}Co(NO_3)_2$ HNO_3 λ	5.45 0 *A*	.0545 0 *A*	.0545 13.72 *A*
690.0	66.9	84.1	69.3
669.0	51.4	66.6	55.9
650.0	40.9	57.8	46.1
632.5	35.5	54.8	44.9
616.5	32.2	51.1	43.5
602.5	29.4	48.7	38.4
589.6	26.0	41.5	30.5
577.0	20.7	30.6	20.4
564.5	12.4	19.5	12.4
553.5	—	—	
543.5	5.56	6.96	5.15
534.0	—	—	
525.0	3.40	4.64	3.35
517.0	—	—	
509.0	3.19	4.49	3.04
479.5	4.23	5.51	4.40
456.0	4.95	7.39	5.56

Graham introduces a classification of hydrates (referring to crystals), calling some of the water molecules water of constitution and other molecules water of crystallization.[22] The only distinction he makes between the two kinds of molecules is that the water of constitution is not supposed to effect the color. Could the new unstable hydrates fall into this class? MacGregor[23] discusses theoretically the variations of water solutions of salts with

temperature and concentration from the standpoint of the gas theory. He concludes that there are a number of molecules of water grouped around (probably not in) the salt molecule and form a complex whole, which he calls a physical hydrate to distinguish it from a chemical hydrate. He notes that an increase of temperature or of concentration decreases the amount of water grouped with the molecule, which, in a measure, predicts the results of Jones. He also states that an increase in temperature will have the same effect upon absorption as an increase in concentration when the concentration is moderate, but will have an opposite effect to change in concentration when the latter is very great. I interpret this to mean that the temperature coefficient changes sign at a certain concentration. Such a test would be interesting, but would not be so very conclusive if it was verified. According to this theory, MacGregor states that the water exercises no particular absorption on account of its transparency. The absorption is to be attributed to the molecular hydrates of the salts or to the dissociation products.

IV. The Cobalt Solutions.

The spectrum of the water solutions of cobalt have a common absorption band beginning between the *C* and *D* Fraunhofer lines, and extending as far as examined nearly to the *G* Fraunhofer line. The maximum absorption is located about 525 λ. The dilute solution of the sulphate, nitrate and chloride, are not as near equal in this band as was observed for the corresponding copper salts in their common band. Still they are near enough to indicate their equality with reasonable certainty for identical concentration in solutions of greater dilution. From the *C* line toward the red limits of the spectrum, the nitrate shows rapidly increasing transparency. The sulphate shows another absorption band in the red with maximum absorption poorly defined and increasing in transparency toward the red limits and transparency possibly as great as the nitrate. The absorption of the chloride in the red is so large as to leave a small transmission band in the orange, which suggests two overlapping absorption bands. Beside the broad red band, there are two well defined sharp bands nearly as narrow as lines in the dark red. These lines or bands are too narrow to indicate their

presence in spectrophotometric observations, but the author has not observed lines between *G* and *F*. A prominent feature of the process of dilution is the rapid diminution of this band in the sulphate and chloride, *i. e.*, the product which causes this absorption is rapidly disappearing, and with great dilution there might be expected an identical curve throughout this part of the spectrum as well as in the common band region. The molecular absorption in the band region is greater than the ionic. The chloride shows the greatest difference between molecule and ions, the nitrate next and sulphate least. This is the order in the copper salt solution, except in the latter the sulphate difference is zero or nearly so. Dilution in the salts increases transparency in all parts of the spectrum. The action of nitric acid in depressing the ionization is marked. One, however, should have anticipated greater effect.

The action of hydrochloric acid upon the chloride was more apparent, but slight differences in the concentration of the acid changed the transmission coefficient appreciably. A trial of the effect of sulphuric acid upon cobalt sulphate gave increased transparency. It was thought that this action was due to slight precipitation, and this surmise was later verified. The color changes of cobalt chloride upon dilution and the changes attending the mixture of cobalt chloride with salts and with hydrochloric acid are well known and have recently been the subject of renewed discussion by Hartley[3] and Donnan and Bassett[20] and more recently by Lewis.[19]

Hartley[3] examined hot and cold solutions of cobalt chloride and regards the phenomenon as explanable upon the "old hydrate" theory, and Lewis[19] contends for the "new hydrate" theory. The latter fails to discuss the previous observations of Donnan and Bassett,[20] whose method leaves scarcely a doubt of another product in solution, which would give the action noted by Lewis. Donnan and Bassett always used concentrated cobalt chloride in their mixtures. Their method is an electrical one and establishes the presence of a complex anion of cobalt in these solutions. The method causes the cobalt to migrate against the current, from a mixture of cobalt chloride in hydrochloric acid, into a hydrochloric acid solution. A blue color is formed similar to the blue of the mixed so-

lution. They compare the color with cobalt chloride in water solution and conclude the product also present in the solutions of Hartley. No photometric measurements are made, and just here Hartley had noted a difference in colored acid solution and colored hot-water solutions. This fact leads Hartley to comment "that to compare mere similarities of color is a less precise method of examination than that of observing absorption spectra through varying thicknesses of solution, and can give but little evidence of chemical constitution unless the color is very marked and practically identical with those already known and capable of identification by their color." This is not valid for indication and proof that a complex colored ion is present in solution. Because if cobalt migrates against the current it is carried as a complex anion. Recognizing this, Hartley admits a possible complex ion in their solution, stating "that Faraday had shown that when fused stannous chloride was electrolysed, stannic passed to the anode, and stannous to the cathode." He further adds that the spectra of the various solutions of cobalt chloride at 23° C., 33° C., 43° C., 53° C., 73° C. and 93° C. are none identical with the anhydrous cobalt chloride dissolved in hydrochloric acid or in alcohol. This same class of hydrates is assumed in the work of Vaillant.[6] If the complex product noted by Donnan and Bassett was present in their experiments, its presence will explain the action noted by Vaillant. As will be seen later, the color of cobalt solutions depends almost entirely upon the concentration of acid at least as long as the cobalt is dilute. Consequently to add cobalt in small quantities directly or through action of an electric current would give blue color, the tint depending upon amount of acid and intensity upon amount of cobalt, and a spectrophotometric examination could tell only what the unaided eye can infer, *viz.*, that cobalt is present, but in what form is a matter of inference from its anionic character. It is perhaps well also to note in this connection concerning the discussions of both Donnan and Bassett, and of Hartley, and of the work of Vaillant,[6] that it is possible to emphasize too much an identity or lack of identity of the absorption of a substance in different solvents. Kundt's law[8] requires a displacement of the absorption band upon change of solvent. Experiments have shown such changes, but

sometimes in the direction opposite to the requirements of the law. It is not permissible to say that a hot cobalt chloride solution in water has the same composition as an anhydrous cobalt chloride solution in alcohol or hydrochloric acid, even if the absorption should prove identical. Likewise their non-identity is not proven by a different absorption. It may be questioned whether a difference like that between Hartley's absorption of cobalt chloride in hydrochloric acid and in water at 93° C. is not of a character which arises from a change of solvent only. Hartley only gives a curve for one concentration of hydrochloric acid, and notes that the color of the cobalt solution does not change upon adding more hydrochloric acid. Just how he makes this change is uncertain. If he means that by adding hydrochloric acid without changing its concentration in solution with respect to water, I have verified it. But this is in reality only a change in the concentration of the cobalt chloride. But if there is a change in the concentration of the acid with respect to the water the changes later noted in this paper are enormous and show that color depends upon the concentration of the acid only, and remind one very much in their character of changes upon heating the water solutions, where color depends principally upon the temperature. As noted, a general similarity or considerable difference will not unqualifiedly prove or disprove a difference of composition. The evidence to the author's mind is at least suggestive of a similar process, in the acid and water solutions, and a product as indicated by Donnan and Bassett.[20]

The increase in transparency of the cobalt chloride in the red upon dilution, as shown by the recorded readings in Table VII., and by two observations (not repeated) for two intermediate concentrations, shows changes out of proportion to the change from molecular to the ionic condition, as noted in the copper chloride studied by Müller.[16] Lewis[19] would attribute this to hydrates, which is a rather improbable supposition. One may as readily assume that there are here complex ions which disappear rapidly upon dilution. This would be in keeping with the observations of Donnan and Bassett. Such a complex ion is also suggested by the observations of Bien[21] upon the transport numbers of cobalt chloride. He found a transport number for a .1 per cent. solution of

TABLE VII.

$\frac{1}{2}$ $COCl_2$.

$\frac{1}{2}COCl_2$ Added Component.	6.80 0	.034 0	$\frac{1}{2}$ ($ZnCl_2$) .017 5.95	.017 10.6	NaCl .017 .545	.017 5.45	NH_4Cl .017 .524	.017 5.24	HCl .0068 .034 4.96	.0034 .017 5.75	.0034 .017 6.51	.0034 .017 7.12	.0034 .017 8.74	.0034 .0068 10.8	.0034 12.1
λ	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*
713.5	8.91	49.5	—	—	—	—	—	—							
690.0	6.61	43.9	29.2	27.0	36.6	26.7	39.5	23.8	30.7	—	—	—			
669.0	6.72	40.4	26.3	23.8	33.3	24.1	36.4	20.5	24.8	4.74	.99	—			
650.0	7.93	39.4	25.8	22.8	33.0	23.7	35.1	20.2	24.5	4.52	.96	—			
632.5	8.36	42.5	26.7	23.7	36.0	25.1	37.3	22.7	25.2	4.88	1.20	—			
616.5	9.32	45.7	28.2	24.7	40.8	27.2	40.4	25.0	28.7	6.20	1.35	.594			
602.5	10.40	47.6	29.7	25.5	43.0	29.2	44.0	25.9	31.6	6.85	1.63	.664			
589.6	9.63	43.4	24.7	21.5	36.5	22.3	37.8	21.2	35.9	8.53	2.39	1.16	.395	.378	(.368)
577.0	7.21	31.4	19.5	15.5	28.0	16.1	27.3	14.7	35.4	10.1	4.09	2.47	.817	.527	(.414)
564.5	5.10	19.65	13.4	10.5	19.0	9.64	19.1	9.12	26.7	9.26	5.57	3.39	1.55	.85	(.738)
553.5	3.86	12.56	96.3	8.15	12.4	7.86	12.5	6.36	17.7	7.27	4.58	3.46	2.42	1.86	(1.62)
543.5	3.06	8.40	6.71	5.69	6.98	4.99	7.07	4.79	9.86	5.72	3.73	3.15	2.59	2.51	(2.40)
534.0	—	—	5.43	4.48	6.16	4.10	6.26	4.00	5.75	4.07	3.13	2.76	2.50	2.45	(2.40)
525.0	2.39	5.01	4.58	4.09	5.25	3.68	5.38	3.63	—	2.85	2.57	2.47	2.25	2.37	(2.30)
517.0	—	—	4.25	3.93	4.81	3.63	4.98	3.69	3.62	2.85	2.45	2.34	2.26	2.29	(2.25)
509.0	2.40	4.82	4.28	4.00	4.85	3.79	5.02	3.77	—	2.85	2.50	2.50	2.60	2.74	(2.80)
501.5	—	—	4.49	4.23	5.01	4.04	5.19	3.95	3.55	2.90	2.73	2.69	2.95	3.30	(3.65)
414.0	—	—	4.98	4.76	5.33	4.43	5.36	4.37	—	3.05	3.12	3.00	3.40	3.81	(4.2)
479.5	3.07	6.15	—	—	6.10	5.80	6.32	5.17	—	3.32	3.49	3.47	4.30	4.65	(5.15)
456.0	4.77	7.82							4.58	4.10	4.31	4.26	5.07	6.21	(6.95)
436.0	7.73								5.66						

cobalt chloride at 18 of .404 for cobalt. When this concentration was 49 times as great and the temperature 27° C., the transport number was reduced to .264. This is readily explained by the presence of a complex anion of cobalt, in the stronger solutions migrating against the current.

When the mixed solutions of cobalt chloride, with sodium chloride, ammonium chloride, and zinc chloride are compared with the cobalt chloride diluted in water only, a marked repression of the dissociation is noted. This seems to be in all cases much less than should have been anticipated by the law of mass action. The more dilute sodium chloride solution contained about 31 times as much chloride as the cobalt. However it is the quantity of anions that determines the repression of the dissociation. The sodium chloride is less dissociated than the cobalt and the ratio for the corresponding ions falls much below 31. Fach of the salts of sodium and ammonium chloride was tested in two concentrations — the stronger ten times the weaker. In the weaker solutions the sodium chloride depresses the dissociation more than the ammonium chloride. In the stronger solution the phenomenon is reversed. This apparent anomaly was explained when a comparison of the electrical conductivities of these salts was made. In the weaker solution sodium chloride is nearly twice as good a conductor as ammonium chloride. In the more concentrated solution the conductivity of the ammonium chloride is over 1.8 times that of the sodium chloride. The zinc chloride also shows depression of the dissociation, but less for the same concentration than the other salts. Donnan and Bassett[20] state that "red aqueous solutions (of cobalt chloride) may be turned blue by the addition of chlorides of metals of pronounced basic function, chlorides of magnesium and calcium are very effective." . . . "Chlorides of potassium and sodium appear to be not so effective. Chlorides of zinc, mercury, antimony, tin, etc., act in opposite manner, *i. e.*, if added in sufficient quantities turn blue solutions, red, whether the blue solution is obtained by increased temperature or by added salt." The observations here recorded indicate the opposite action of zinc chloride. Donnan and Bassett[20] were, however, dealing with concentrated cobalt chloride. They explain this phenomenon on the assumption of a complex ion of the form MB_3''

or MB_4'' for these bivalent metals transparent for all of them except cobalt chloride; and it having strong absorption in the red. The normal ion is then supposed nominally transparent in this region. Supposing that to M''-MB_3'' colored, is added M'', MB_3'' transparent, in such a way as to increase quantity of negative ion. The equations for mass action requires that MB_3'' colored diminish, *i. e.*, in this case the solution becomes red. Whereas if to M'', B'' dilute, is added another component containing M'', B'' and some reaction takes place between the latter component and dilute solution. Some of the MB molecule is formed; and from the MB molecule, there will be produced some M''-MB_3''. In the case of the chloride of cobalt this product has absorption in the red. In this case then the cobalt solution becomes less transparent in the red as in the above observations. For the observations with the present added salts taken alone, there is no need of any assumption of more than simple ions. If the color changes produced by these salts arose from the hydrates of Jones and Bassett,[18] the greatest change should have been produced by the zinc chloride instead of the least as observed. The same statement holds for the added sulphate salts.

The addition of these salts never sufficed to restore the partially dissociated cobalt solution to the condition of the concentrated solution. When mixtures of hydrochloric acid and cobalt chloride, however, were studied, it became apparent that the original condition was restored when about 5 equivalent of the acid was used. Further addition of acid did not bring the data to the ultimate limit of ions restored to the form of cobalt chloride molecules, but caused more marked changes than ever. Every addition of acid increased the absorption in the red and transparency in the violet. This indicates a new product and possibly a product also present in considerable proportions in the original concentrated solution, and possibly the complex ion indicated above. It may also mean a change in solvent. It may mean both of the changes combined. It was found that the absorption did not depend upon the concentration of the dilute cobalt solution but upon the concentration of the acid, *e. g.*, maintaining the acid constant and varying the concentration of the cobalt five fold did not affect the absorption. This fact would generally be fatal to the complex anion hypothesis. But when we con-

sider that the smallest ratio of hydrochloric acid to cobalt chloride is three hundred, the transformed portions might in all solutions be so near equal that no difference could be detected. However, a change in the acid of a small percentage produced a marked effect upon the color. For example in a solution containing $x\mathrm{C_0Cl_2}$, $y\mathrm{HCl}$, and $z\mathrm{H_2O}$, where x is small, a variation of x, five fold, gives identical equivalent transmission coefficients. A change of a few per cent. of y, and x varying as before, gives another set of coefficients all falling upon another curve. If it is a question of mass action, this difference should not have been noted, as the ratios of x to y in the two sets of readings are in some cases identical. The phenomenon is, however, explicable upon the hypothesis of a change in the solvent from water to hydrochloric acid. Suppose a substance A, soluble in B and also in C, and nothing whatever said as to the form of the A product in B or in C. Let the A-B mixture be red and the A-C mixture blue, so that their transmission curves form a cross like the letter X. Their transmission curves then intersect at some point in the spectrum. If parts of A-B and of A-C be placed in the path of the light a transmission curve will be obtained intermediate between the two and intersecting at their common intersection. The curve will be nearer to A-B or A-C, according to which is used in greater quantities. This will not effect the transmission coefficient through all ranges of values for A under saturation and constancy of the product A. Neither will it be affected if A takes the form A-B, *e. g.*, simple ion, molecule or hydrate, and A-C, *e. g.*, complex ion or complex molecule. All the curves, after 6.5 equivalents of hydrochloric acid are added, which one may regard as having removed dissociation, are included between two such extremes, and as nearly as could be expected intersect in a common point. The actual intersections lie between 525 $\mu\mu$ and 515 $\mu\mu$. The writer fails to see wherein the argument is invalidated if the solvents, hydrochloric acid and water are miscible in all proportions.

In the study of cobalt sulphate the addition of $\mathrm{ZnSO_4}$ caused an increase in transparency. There was a suspicion of slight precipitation in the solution as there had been in the case of cobalt sulphate, sulphuric acid solutions. It was thought that this could

possibly arise from the total concentration of SO_4'', exceeding the saturation value for cobalt sulphate. The concentration was therefore taken below this limit. The result is given under $\frac{1}{2}(ZnSO_4)$ of concentration 4.742, Table VIII. This gives a diminution of the section, but increased transparency is still present. Since this action extended through the spectrum (blue readings are marked uncertain and not recorded) and not limited to one color, the writer still clung to the idea of a slight precipitate. The zinc sulphate was accordingly reduced to .114 equivalent and another test made. This concentration yielded results similar to results in cobalt chloride and mixed salts. This result is, however, much less pronounced. However, this was to be expected, as the cobalt sulphate changes upon dilution are much smaller than those of the chloride. It was not so difficult to prove the formation of a precipitate in the sulphuric acid solutions. By increasing the acid strength the precipitate was soon marked enough in the bottom of a beaker to recognize. Another phenomenon is worthy of notice. If strong sulphuric acid is added to a moderately concentrated water solution of cobalt sulphate, a precipitate soon forms which is redissolved upon further addition of acid. The deep red color is characteristic of the latter solution. The writer wasted 70 per cent of his observations upon this mixture before he fixed the inconsistencies of obervations upon this kind of a change in the dilute solutions of cobalt. He had thought the difficulty in the diffuse radiation (before mentioned) to arise from small air bubbles in the acid, a difficulty always present, and hiding the serious difficulty by the diffusion. The precipitate in suspension even in minute quantities darkened the whole field, but more especially the red. When precipitated it removed an appreciable portion from solution, giving abnormally high transmissions. When redissolved it had another color. Given these three factors at once, and the shaking which arises from repeated handling of tubes during observations, the possibilities of inconsistency are apparent. The difficulty was solved by further diluting the cobalt sulphate. The concentration used with the zinc sulphate mixture was about the maximum that could be used with a 50 per cent. sulphuric acid solution without complication. For the strongest acid a dilution about five times this is necessary. These statements

TABLE VIII.

½ $CoSO_4$.

½ $CoSO_4$ Added Component.	4.85 0	.0485 0	½ $ZnSO_4$ .0485 5.69	.0485 4.74	.0485 .114	½ H_2SO_4 .0485 12.77	.0278 19 6	.0243 21.3	.006 .012 24.6	.006 .012 28.6	.006 .018 32.2	.006 .012 34.83	.006 .012 35.42
λ	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*
713.5	—	68.3	—	—	56.0	—	—	—	—	—	—		
690.0	45.6	58.0	75.9	62.1	51.0	(44.1)	48.9	(58.0)			(78.0)		
669.0	38.9	54.6	66.3	57.4	46.4	42.3	45.1	—	67.6	69.8	76.1		
650.0	37.9	49.3	58.3	56.5	46.8	41.5	46.5	52.6	67.6	67.2	74.0		
632.5	36.5	49.2	52.9	53.2	47.5	—	47.4	—		48.0	48.8	(80.0)	20.0(?)
624.0	—	—	53.7	53.7	—	—	—	—	58.4		—	—	38.8
616.5	39.6	50.6	55.2	54.2	47.8	42.6	49.2	46.8		22.8	21.9	21.0	20.7
609.0	—	—	—	—	—	—	—	—	—	—	—	—	13.5
602.5	41.5	50.8	51.5	50.0	43.3	48.5	45.1	48.0	36.0	12.5	10.0	9.52	8.86
595.5	—	—			—	—	—	—	—	—	7.32	—	6.45
589.6	37.7	45.6	35.1	37.9	32.4	29.6	27.2	25.2	18.8	6.10	5.49	5.82	4.80
577.0	25.3	34.0	24.5	—	20.1	19.9	19.1	10.5	9.35	4.27	3.30	3.22	3.62
564.5	—	21.0	—	19.3	—	12.6	12.3	6.39	5.47	2.94	2.80	2.72	2.56
553.5	—	12.4	12.5	—	12.5	7.30	7.50	4.37	4.10	2.48	2.37	2.25	2.10
543.5	6.91	7.86	8.8	7.64	—	5.73	5.50	3.42	3.35	2.40	2.24	2.12	2.01
534.0	—	—				4.43	4.40	2.97	3.02	—	2.22	2.22	1.98
525.0	4.43	4.90				3.82	3.80	2.83	2.80	2.38	2.27	2.38	2.18
517.0	—	—				—	3.81	—	—	—	2.50	—	2.48
509.0	3.90	4.62				3.71	3.88	2.88	3.13	2.99	2.95	3.18	2.78
494.0	—	—				4.15	4.92	3.46	3.92	3.33	—	4.21	3.22
479.5	4.78	6.10				4.72	6.45	3.82	4.87	4.11	5.64	6.15	4.45
467.5	—	7.35				—	—	—		5.12	—	—	—
456.0	6.35	—				6.6	9.90	6.28	6.34	—	9.04	—	7.76
436.0	11.2	10.0				11.6	—	9.63	10.1	—	10.8	—	8.90

are not made to imply the limit of solubility of cobalt sulphate in mixtures of sulphuric acid and water, but the limits found necessary for consistency in repeated measurements.

The data ultimately secured, possess some common characteristics with the chloride of cobalt in hydrochloric acid. The acid first represses the ionization, partially or completely. Then further addition causes a marked change in the absorption and shows a shift of the band. The final curve clearly corresponds to a solute in a new solvent. All curves lie between the two extremes. The conditions here do not, however, give a common point of intersection. The absorbent in water has its main absorption in the green, but a minor absorption band appears in the red, with a slight diminution in the orange. The absorbent in sulphuric acid has but one band. It is more intense than the main water absorption band and is shifted toward the yellow with respect to the latter band. The absorption diminishes so rapidly toward the red, that, at about 625 $\mu\mu$ its curve crosses the water absorption nearly at right angles. The point of common intersection is not so well defined as in the case of the cobalt chlorides. Curves No. 10, 11, 12, and 13, Fig. 7, intersect in a region where the slope is very steep. Within the limits of accuracy their common point could be at their intersections with 1, 6 or 7. The two points missing, see Table VIII., for curve 8 are badly needed. This curve may intersect with 7 and 10, 11, 12, and 13. This point would then lie considerably higher than an intersection with a curve of no ionization in a water solution. Naturally this latter curve would lie below 1 rather than above both 1 and 6. By putting the common intersection as low as curve 1, curves 7 and 8 do not represent progressive changes from 1 toward 13. In this region curve 9 is very irregular. Then, although there is a moderately well defined place of intersection it is not so well defined as in the chloride and the complexity suggests the presence of some other components. The data also indicate an intersection of the curves in the blue end of the spectrum, but this, even if true, is not well enough defined to follow with accuracy.

There seem to be indications of such an action present in the mixed solutions of copper bromide in water and in alcohol, and possibly in some other mixtures of Vaillant's investigations.[6] His

spectrophotometric measurements are not complete enough to prove it, but are adequate to suggest it. For example, he observes absorption extremes for water and alcoholic solutions and for mixtures of the two solvents in a small portion of the spectrum. These mixtures have intermediate values and hence his assumption that the mixtures give absorption which is determined by the ratio of the absorption of the salts in the two solvents.

Résumé.

1. The spectrophotometric study of solutions of copper chloride, copper sulfate, copper nitrate and copper acetate has been made in more extended portions of the spectrum and in widely varying concentrations.

2. A spectrophotometric study of cobalt chloride, cobalt sulphate and cobalt nitrate is given in concentrated and in dilute solutions.

3. Beside the ordinary method of treatment, salts and acids are added to repress the ionization.

4. Ostwald's law that dilute solutions containing a common colored ion have a common color, is confirmed.

5. The dynamic law of mass action between ions is clearly confirmed by the diminished association due to added salts and acids which contain a common ion.

6. There has been no evidence gathered showing the presence of hydrates in solution having water added to the molecule and the whole playing the role of a molecule. A hydrate which is a physical aggregate of salt and water and not a molecular combination, may possibly be revealed by a thorough comparison of electrolytic, freezing point, and spectrophotometric data. The latter can be studied as in this paper but must be more complete.

7. There is some evidence (but needing a larger study) of complex anions of cobalt, in cobalt chloride water and acid solutions, with both water and acids acting as solvents. The phenomena in copper chloride may be similar to those in cobalt chloride, and a satisfactory explanation of the changes in the one will probably cover the changes in the other and in similar solutions.

8. The addition of strong acids to cobalt chloride and cobalt sulfate suggests a change of solvent. The character of the data suggests a solute distributed between two solvents, miscible in all pro-

portions, without any assumption as to the phase of the solute. This process seems well-defined in the chloride and has some complications in the sulphate.

9. There is a marked displacement of the absorption band upon a change of the solvent.

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SPARK POTENTIALS IN LIQUID DIELECTRICS.

BY ROBERT F. EARHART.

AN extensive literature exists on spark potentials. This is confined, for the most part, to a study of gaseous dielectrics.

In this paper spark potentials, for small distances, in liquid dielectrics are discussed. Extended experiments on the disruptive strength of various oils, used in the insulation of electrical machinery, have been made by several of the companies engaged in the manufacture of such apparatus. No doubt, much interesting matter, so secured, has not been published by the investigating parties.

In the recent publication, Turner and Hobart on the Insulation of Electrical Machinery, various sections deal with the disruptive strength of oils. For the most part, Mr. C. P. Steinmetz is quoted as authority. In the original paper of Mr. Steinmetz,[1] measurements on the potential required to cause a spark to pass between parallel plates are given. These measurements were made with a periodic P.D., an alternate current transformer being used to obtain the required P.D.

The results obtained by Mr. Steinmetz do not agree with those obtained by MacFarland and Pierce.[2] The last named investigators obtained their P. D. from a Toepler-Holtz machine. They experimented on a large number of oils and are the authorities quoted in the Smithsonian Tables edited by Dr. Thomas Gray. In a discussion of the various results obtained,[3] Dr. MacFarlande points out that the method employed by Mr. Steinmetz in measuring distances, interrupted the continuity of the liquid and explained the discrepancy on that ground. In the Steinmetz experiment, two plane electrodes were separated by a solid dielectric, of known thickness, containing a hole. This aperture contained the oil

[1] Proc. Am. Inst. E. E., 1893, p. 85.
[2] PHYSICAL REVIEW, Vol. I., p. 165.
[3] Proc. Am. Inst. E. E., 1893, p. 109.

through which the spark passed. Mr. Steinmetz maintains that values of spark potentials obtained by the use of static machines do not afford data which the electrical engineer can accept. Both agree that the electrostatic potential gradient required to cause the passage of a spark between electrodes is constant, although they do not agree upon the value of this constant.

That this not true for air and other gases has long been known, the potential gradient decreasing with increase in distance. Mr. Steinmetz calls attention to the fact that if the curves showing the relation between potential and distance be plotted, an exterpolation of these for air and the various oils, would give a higher potential gradient for air if the distances were small. His computed value for air, at small distances, gives a gradient of 139 kilovolts per cm. and he calls attention to the fact that this is about the value obtained for red fiber and is higher than for any of the oils on which he operated.

The author has made a series of observations on spark potentials in air and CO_2, for extremely short distances.[1] The results for air at atmospheric pressure are shown, for purpose of comparison in Plate II. The values obtained were for P.D.'s from a bank of storage cells. In a later paper,[2] similar and almost identical results were reported as secured from an A.C. source. The interesting part of this curve lies in the peculiar bend occurring at a distance of approximately 3 micra and for a potential of about 350 volts. This indicates a change in the law at this point and the value 350 volts corresponds with what is commonly termed the minimum spark potential of air.

Professor J. J. Thomson[3] explains this turning point on the theory that for potentials less than this critical potential, the discharge is carried by free metal corpuscles projected from the electrodes; that for greater potentials both metal corpuscles and ions of the dielectric are the carriers.

In the present experiment, it is desired to extend spark potential curves over extremely small distances, using liquid dielectrics. The

[1] Phil. Mag., 1900, p. 147.
[2] PHYSICAL REVIEW, VOL. 15, p. 163.
[3] Conduction of Electricity through Gases, p. 384.

distances cover a range from .118 mm. to .003 mm. and are thus comparable with previous measurements in air.

CONDITIONS WHICH AFFECT SPARK POTENTIALS.

In such measurements there are a number of variables which must be taken into consideration. The P.D. required to cause a spark between electrodes depends: (1) Upon the distance separating the electrodes, (2) upon the nature of the intervening medium, (3) upon the pressure, (4) upon the temperature, (5) upon the length of time of application of P.D., (6) upon the shape and size of the electrodes, (7) in case the electrodes are not of the same shape, upon which one is positive, (8) upon whether the intervening medium is ionized by the action of Roentgen rays or other means, (9) upon the material of which the electrodes is composed, (10) upon the strength of the magnetic field in which the discharge occurs.

The foregoing list may not be complete, but sufficient work has been done by various investigators to show that any of these causes may modify the values obtained. Some of these apply only to particular cases. The relation between distances and pressures for gaseous media is embodied in Paschen's law. This is fully discussed by Carr.[1] The fourth consideration, *viz.*, that of temperarure, has never been fully investigated. Turner and Hobart[2] quote a series of measurements showing variations in the disruptive strength of some commercial insulators, due to temperature changes. Oiled linen, for example, was one of the insulators tested. The results show a decrease in the disruptive strength with increase in temperature. It seems probable that temperature effects would cause greater variations in liquid than in gaseous media.

The influence of time of application of the P.D. was first investigated by Warburg and is commonly known as the lag. The size and shape of the electrodes has been studied by Baille and others. The results obtained by a number of investigators are compared and discussed by J. J. Thomson.[3] The effect of polarity of the electrode seems to be most important in the case of a point and plane.

[1] Proc. Roy. Soc., 1903, p. 374.
[2] Insulation of Electrical Machinery.
[3] Conduction of Electricity Through Gases.

Change of the spark potential due to external ionization of the field appears to be confined to gaseous media and has the effect of diminishing the time of lag.[1] Dr. G. M. Hobbs[2] has investigated the effect of the material composing the electrode on spark potential. He has shown that at the elbow or turn of the potential distance curve in air, that this curve lies parallel to the X-axis for a certain distance and that this distance of parallelism depends on the kind of metal used as the electrode. For distances greater than those represented by the bend in the curve the nature of the electrode appears to have no effect.

The effect produced by a magnetic field is most pronounced in gaseous media under small pressures. Precht[3] has investigated the case for atmospheric pressures under certain special conditions.

If periodic P.D.'s are applied, the introduction of capacity and inductance in the circuit containing the spark gap may introduce resonance conditions. This would greatly modify apparent values of the P.D. when measured by the usual method.

Description of Experiment.

In this experiment the variation of spark potential with distance is treated. The dielectrics used were kerosene, paraffin oil, olive oil and a transformer oil purchased on the market. One surface consisted of a circular plate 3.80 cm. across the face; this was ground plane but not polished. The other surface consisted of a ball 2.54 cm. in diameter. Both surfaces were of steel. Changes in atmospheric pressure were regarded as unimportant within the limit of accuracy of the experiment. The temperature conditions were very favorable. The mean temperature was 21° C., with variations of not more than one degree. The apparatus was so constructed that only a small quantity of oil was used at one time. The oil was obtained in sufficient quantity and renewed after each discharge. It is believed that this precaution is unnecessary. This point will be discussed later. For measurements on potential through small distances, it is necessary to measure both distances and potentials ac-

[1] Warburg, Wied. Ann., lix., p. 1, 1896.
[2] Phil. Mag., December, 1905, p. 617.
[3] Wied. Ann., 1896, p. 676.

curately. Distances were measured by attaching the plane surface to the movable arm of an interferometer from which it was insulated. The ball was insulated from and suitably mounted on the interferometer bed. The surfaces were then brought in contact and separated. The distance of separation could be determined by the number of light fringes, preferably circular, which crossed the interferometer field during separation of the surfaces. Sodium light was used, and from the known wave-length of the sodium radiation, distances were determined. The arrangement as indicated in Fig. 1 D and D' indicate the surfaces, M the mirror on the carriage of the interferometer. The vessel containing the liquid is designated V.

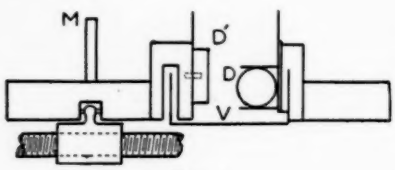

Fig. 1.

The ball and plate were so mounted that fresh portions of the surfaces could be brought into contact after each discharge. The point of contact was determined by a galvanometer and small E.M.F. No difficulty was experienced in securing a positive and definite zero setting. P.D. was measured by means of a Weston A.C. voltmeter, properly calibrated, and reading directly to 120 volts. By means of suitable multipliers, potentials up to 1,500 volts could be measured. The result in root of mean square volts can be transformed into maximum volts by multiplying by the proper factor. If we assume a sine form wave this factor is 1.41. Oscillograph curves of the E.M.F. show that a sine form is only approximated. The departure of this curve from a true sine form is such that variations in the readings obtained will hardly justify a further refinement in the matter of correction.

P.D.'s were obtained from a bank of incandescent lamps arranged in series. A General Electric transformer took current from a 110-volt 60-cycle circuit and stepped it up to 2,200 volts. This was passed through a bank of 44 incandescent lamps arranged in series. By introducing suitable lead wires, it was possible to utilize the fall in potential across one or more lamps. The transformer could be connected to give a total fall in potential of 550, 1,100 or 2,200 volts. Smaller steps than the direct drop across lamps could be

obtained by shortcircuiting lamps outside the lead wires or by throwing lamps in parallel inside the lead wires. The small capacity and induction of the lamp filaments makes this a desirable means of obtaining P.D.'s.

Fig. 2 shows the manner of applying the P.D. to the electrodes D, D' across which the voltmeter V was connected. A suitable double-throw switch was arranged so that the galvanometer G could be placed in circuit to test for contact, or a P.D. applied.

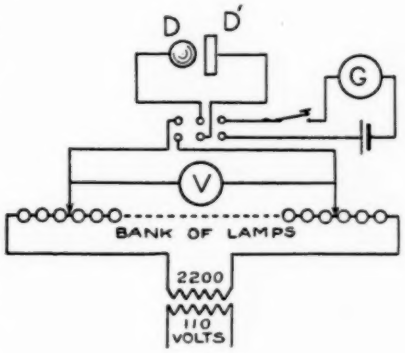

Fig. 2.

The method of procedure was to separate the surfaces a known distance and apply P.D.'s building up by small increments. The P.D. was applied for 5 seconds. If the medium did not break down a higher P.D. was applied and so on until a spark passed. This would be indicated by the deflection of the voltmeter needle.

The tables indicate both the values which the dielectrics would withstand and those at which they broke down. These are indicated on the graphical representation by a cross and circle, respectively.

Results.

Plate I. (Fig. 3) represents graphically the results obtained on a transformer oil. This was purchased from a local concern as a low grade transformer oil.

This shows a bend in the curve corresponding to approximately 350 volts and at a distance lying between 13 and 15 micra. For distances below this elbow, the passage of a spark always produced coherence between the surfaces. No matter for how brief a time the P.D. was applied, a test with the galvanometer showed metallic contact between the surfaces. For distances above this bend such was not the case. The appearance of the surfaces in the two cases was noticeably different. For potentials corresponding to the flat portion of the curve, no discoloration of the surfaces or carbonizing

TABLE I.

Transformer oil.

Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke.	Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke.
5	115	123	35	372	395
10	191	206	40	412	423
15	226	259	45	395	412
15	268	288	45	406	423
17.5	305	310	50	434	457
20	327	350	60	457	468
20	310	327	70	468	485
22.5	338	364	80	496	507
25	350	388	90	455	502
25	310	344	100	558	575
30	384	395	150	609	635
30	372	406	150	651	668
35	372	395	200	871	888

of the oil was observed, for distances greater than this critical distance both surfaces and oil were badly discolored and the surfaces pitted. This is characteristic of all the oils operated upon. Fresh oil was used after each discharge.

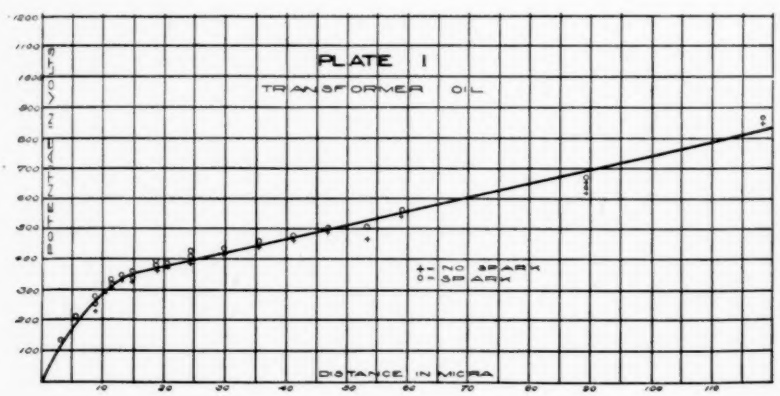

Fig. 3.

A series of readings was taken to determine if changes in the disruptive strength occurred after the passage of a spark. The results are shown in Table Ia.

In this case the surfaces were separated a distance of 40 wave-lengths (Na Light) or approximately 24 micra. The first reading was taken on a fresh oil, the second after a spark had passed during the time a switch could be closed and opened by the hand. This

TABLE IA.

P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.	Condition of Medium.
406	423	Fresh oil.
412	423	Quick spark.
406	420	Quick spark.
406	417	Spark had passed 30 sec.
406	429	Spark had passed 60 sec.

is designated as a quick spark. From the foregoing results, it would seem that the precaution of using a fresh oil after each discharge is unnecessary and that the oil is self-healing. The entire curve was repeated without renewal of the oil and practically the same results obtained. A second transformer oil sent out by one of the large electrical manufacturing companies gave the same result within the accuracy of the experiment.

Table II. gives the results secured with kerosene oil. This was a high grade resistance kerosene. The results are given graphically in Fig. 4. A similar curve for air at atmospheric pressure is also

TABLE II.

Kerosene.

Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.	Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.
5	79	110	35	417	451
5	56	112	40	389	411
7.5	129	136	45	—	451
10	182	203	50	423	451
10	169	226	60	451	474
12.5	268	299	70	451	474
15	268	299	80	552	564
17.5	322	328	90	564	592
20	327	347	100	592	620
25	350	389	150	810	850
30	389	411	200	980	1,020

given. It is interesting to note that, for the distances taken, air is the better insulator. Mr. Steinmetz' prediction on this point has been noted previously. It is well known that the air curve bends toward the X-axis and it is presumed that the curve representing

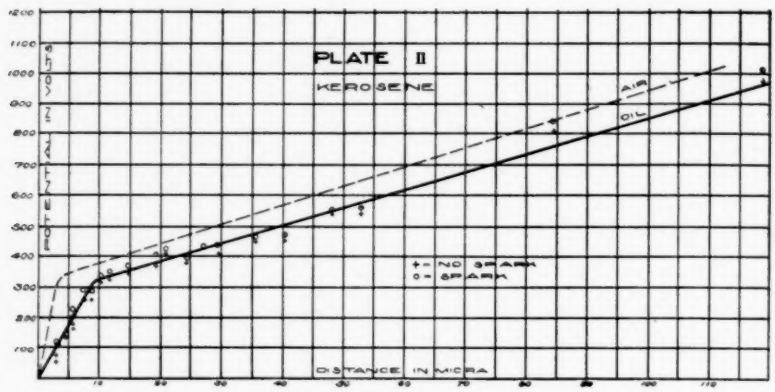

Fig. 4.

the disruptive strength of a liquid is a straight line. At the point of intersection the spark-potentials would be equal. MacFarlande and Pierce[1] gave this as 1 mm. for air and kerosene.

If this curve for kerosene is exterpolated the potential gradient at 1 cm. would give 55 kilo-volts per cm. This requires an exterpolation of the curve to something like 80 times its length and is unwarranted, however, it agrees well with the value obtained by MacFarlande, which was 50 kilo-volts per cm.

Plate III. (Fig. 5) represents the results obtained with paraffin oil. This shows a potential gradient somewhat less than that of kerosene and does not agree with MacFarlande's value of 87 kilo-volts per cm.

Paraffin oil, however, is a trade name applied to a number of the petroleum products. Oils sold under this name vary from heavy viscous oils to extremely limpid ones. The oil operated upon, in this case, was a clear limpid oil prepared by a drug firm and sold to the medical trade under the name of petrolatum oil. It may be observed that the curves representing the petroleum products show similar values and so far as their disruptive strength is concerned one is practically as good as another.

[1] PHYSICAL REVIEW, Vol. I., p. 165.

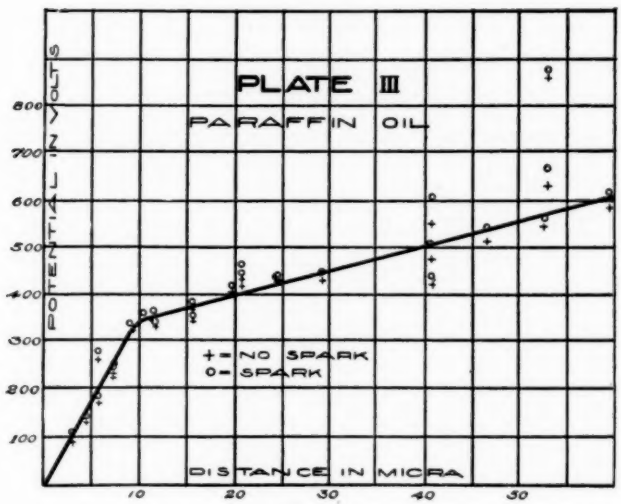

Fig. 5.

TABLE III.

Paraffin Oil.

Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.	Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.
5	92	110	35	434	451
7.5	127	135	40	412	446
10	265	282	40	485	508
10	164	188	45	451	462
12.5	226	254	45	462	474
12.5	234	245	50	412	440
15	327	350	60	479	508
15	311	344	70	479	508
17.5	271	282	70	423	440
17.5	377	389	70	547	609
20	333	344	80	508	547
20	344	361	90	540	558
25	310	338	90	620	661
25	355	378	90	863	884
30	400	411	100	558	630
30	—	406			

Plate IV. (Fig. 6) shows the results secured with olive oil, the only vegetable oil used in the test. It shows a higher potential gradient than any of the others. The bend in this curve is not so

TABLE IV.

Olive Oil.

Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.	Distance in Wave-lengths Sodium Light.	P.D. which Medium Would Withstand.	P.D. at which Medium Broke Down.
5	59	94	30	384	390
5	55	94	35	406	429
7.5	113	118	35	406	446
10	149	164	40	440	457
10	164	169	40	448	468
12.5	175	186	45	491	513
15	175	223	45	505	513
15	155	178	50	550	592
17.5	223	240	60	584	626
20	271	293	70	546	626
22.5	288	310	70	632	643
25	342	388	80	685	711
25	372	384	90	744	792
27.5	388	416	100	792	843

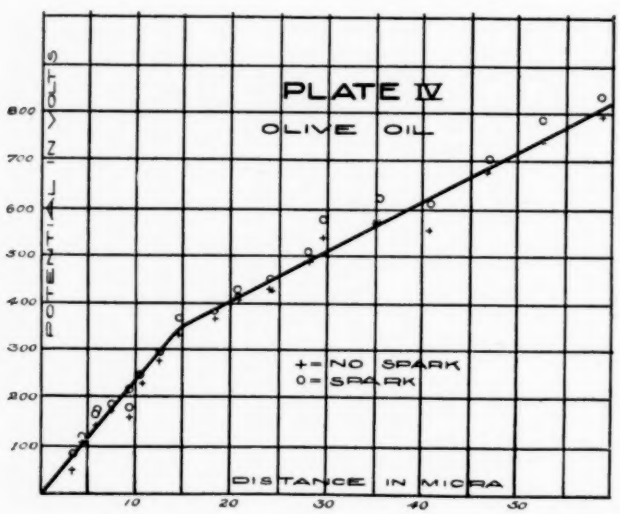

Fig. 6.

apparent. There is some evidence of a turning point at a P.D. of 350 volts, at which coherence between the plates ceased.

An attempt was made to secure readings with water as a dielectric. Platinum electrodes were used in a high grade of ammonia-

free distilled water. This was a complete failure. The problem of securing a suitable water in the quantities desired seems very difficult, in the light of the Kohlrausch experiments on water. The conductivity of this water was not measured on account of the failure to obtain results.

Conclusions.

These experiments on the limited number of oils used would indicate :

1. That the potential gradient for very small distances is higher than for large ones.

2. That for small distances air is a better insulator than liquid dielectrics.

3. That the potential at which the bend in the potential-distance curve occurs is the same for air and liquid dielectrics.

If we accept Professor J. J. Thomson's explanation of the mechanism of spark discharge in gases for potentials less than the "minimum potential," *viz.*, that free metal corpuscles are the carriers of the discharge, and attach a similar meaning to the elbow occurring at the same voltage in liquids, it would follow that the corpuscles were able to travel further in liquids than in gases.

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HYDRATION IN SOLUTION.

BY C. S. HUDSON.

IN the present article the formation of hydrates and their anhydrides in solution is considered and an explanation is attempted of some of the general phenomena of hydration, such, for example, as the occurrence of transition temperatures, the equality of solubilities at these temperatures, and the fact that the stable substance always has the smaller solubility. The explanation that I give of these general facts is based on the observations of the hydration of milk-sugar that I have published.[1]

1. THE RELATED SOLUBILITIES OF A TYPICAL HYDRATE, MILK-SUGAR, AND ITS ANHYDRIDE.

Suppose an anhydrous substance A, for example anhydrous milk-sugar, to form with water a single hydrate H, hydrated milk-sugar. The reaction which takes place in dilute solution between these two substances can be represented by the symbol of a balanced reaction.

$$A \rightleftharpoons H, \tag{1}$$

if the constant mass of the reacting water is omitted for brevity. If the initial solubility of A at a chosen temperature is s_a, and the concentration of H that is in equilibrium in solution with s_a of A is C_h, the final solubility of A is

$$S_a = s_a + C_h. \tag{2}$$

In like manner the final solubility of the hydrate is

$$S_h = s_h + C_a. \tag{3}$$

Since it has been shown by Nernst[2] that the proportion of hydrate

[1] Princeton Bulletin, April, 1902. Zeitschrift für physikalische Chemie, **44**, 487–494 (1903); **50**, 273–290 (1904). Journal of the Americal Chemical Society, **26**, 1065–1082 (1904).

[2] Zeitschrift für physikalische Chemie, **11**, 345 (1893).

that is in equilibrium with anhydride is nearly independent of concentration we may write as a close approximation

$$C_h/s_a = s_h/C_a = K. \tag{4}$$

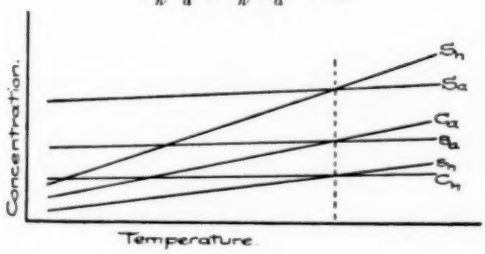

Fig. 1.

In the accompanying figure the quantities that occur in the three equations are represented over a range of temperature. Three of these lines can be drawn at will for a typical substance, but the others are then determined by the positions of these three. I have drawn s_a, s_h and S_h from the solubility data of milk-sugar.

It follows from the equations (2), (3), and (4) that

$$S_a \gtreqless S_h \text{ and } C_h \gtreqless s_h \text{ when } s_a \gtreqless C_a. \tag{5}$$

This relation, and also the figure, shows how it is that one of the substances A and H is stable at a chosen temperature in the presence of water while the other is unstable, and also shows which of the substances is the stable one. Thus, for example, if it is known that $s_a > C_a$ it is to be concluded that the hydrate is the stabler form, for since $C_h > s_h$, the finally saturated solution of anhydride contains hydrate in greater concentration than that corresponding to the initial solubility of the hydrate and is thus supersaturated with respect to the hydrate; on the other hand, since $C_a < s_a$, a finally saturated solution of the hydrate contains anhydride in less concentration than its initial solubility, and such a solution is undersaturated with respect to the anhydride and is stable. Or, briefly, we may say that the stable substance is the one whose initial solubility is greater than its concentration in the finally saturated solution of the other substance. This definition of the stabler substance leads from (5) to the conclusion that the unstable substance in the case of hydrates and anhydrides has the greater final solubility, a

fact that is of the most common experience and which Van't Hoff[1] and Ostwald have proved holds for all substances. It is instructive to notice that though there is the necessity in the definition of the unstable substance that it have the greater final solubility, there is, on the contrary, no such relation between stability and initial solubility. This conclusion is evident when the equations (2), (3) and (4) are reduced to the form

$$s_a/s_h = S_a/S_h(1/K). \tag{6}$$

Since K, the equilibrium constant of the hydration reaction, is not known to depend on the relative stability of the two substances, it is not possible to decide from a knowledge of their relative stability anything regarding their initial solubilities.

2. THE TRANSITION TEMPERATURES OF HYDRATES.

The relations shown by the equations (2), (3) and (4), and represented in the figure, also lead to a simple view of what takes place in a solution of a hydrated substance at its transition temperature. To show this we may first sum up the properties of such a solution that are peculiar to this temperature; they are, equality of the final solubilities of the hydrate and the anhydride, identity of the two resulting solutions, and equality of the vapor pressure of these solutions with that of a mixture of solid hydrate and anhydride. I know of no molecular-kinetic explanation of the last one of these general properties, but the first two receive a clear explanation from the equations and the figure, as follows: At whatever temperature $C_a = s_a$, $C_h = s_h$ and $S_a = S_h$, from (5). At this temperature, therefore, which may be defined the transition temperature,[2] the two substances have the same final solubility and also give solutions which contain the same substances in the same concentrations, and are therefore identical, which was to be shown.

If this is the correct explanation of the peculiar properties of solutions at the transition temperatures we should not expect at these temperatures any sudden or discontinuous change in any

[1] Vorlesungen, 1903, II., p. 127.

[2] It has already been shown by Van't Hoff, Vorlesungen, 1898, I., 219, that at transition temperatures the concentrations of the substances in saturated solution are equal to their initial solubilities.

property of the solution, because the same substances exist in solution below, at and above the transition temperature, and the relative concentrations of these substances change gradually and continuously with the temperature. There is indeed no evidence at all that supports the alternative hypothesis, which is now generally abandoned, that below the transition temperature only the one form exists in solution, and above this temperature only the other form. It is certainly a more rational view to assume that both above and below this temperature both or indeed all forms of the substance exist together in solution, their concentrations and initial solubilities being related in the manner that has been indicated.

3. Thermodynamics of Hydration Reactions.

The solubility relations that are shown by the figure receive additional interpretation from the application to them of thermodynamic principles.

To begin with, let the free energy of the isothermal formation of solid hydrate from solid anhydride and water be calculated. This hydration can proceed reversibly in three ways, namely, by isothermal distillation of water, and by dissolution of anhydride and water in, and crystallization of hydrate from, saturated solutions of anhydride and hydrate respectively.

a. Hydration by Distillation.

If the vapor pressure of pure water at absolute temperature T is p_w and the pressure of the aqueous vapor that is in equilibrium with a mixture of solid hydrate and anhydride is P_h, then by isothermal evaporation of the water, expansion from p_w to P_h, and condensation on the solid anhydride, the hydrate can be produced isothermally and reversibly with the gain per mol of hydrate produced of the work,

$$W = nRT \log p_w/P_h, \qquad (7)$$

where n is the number of molecules of water that occur in the hydrate.

b. Hydration by dissolution in saturated anhydride solution.

Imagine a reservoir composed of a finally saturated solution of the anhydride, containing anhydride and hydrate in the concentra-

tions s_a and C_h respectively. Draw out from this reservoir through a wall that is permeable for the solvent and the hydrate but impermeable for the anhydride one mol of hydrate at the constant concentration C_h, and at the same time allow one mol of anhydride to dissolve into the reservoir and n mols of water to evaporate at p_w, to expand to p_a, the vapor pressure of the saturated solution of the anhydride, and then to condense into the reservoir. The mol of withdrawn hydrate is then to be concentrated from C_h to s_h, the initial solubility of the hydrate, and crystallized from the solution. The final change that is produced by this process is the conversion of solid anhydride and water to solid hydrate because the reservoir remains unaltered, and the free energy of the hydration per mol of hydrate formed is

$$W = nRT \log (p_w/p_a) + RT \log (C_h/s_h). \qquad (8)$$

c. Hydration by dissolution in a saturated hydrate solution.

By a process similar to the foregoing one dissolve one mol of anhydride at concentration s_a in water, concentrate it to C_a, and press it into a saturated solution of the hydrate; at the same time distil n mols of water into the saturated solution and crystallize from it one mol of hydrate. The free energy by this method of hydration is

$$W = nRT \log (p_w/p_h) + RT \log (s_a/C_a). \qquad (9)$$

Since the three expressions (7), (8), and (9) for the free energy are equal it follows that

$$(p_w/P_h)^n = (p_w/p_a)^n(C_h/s_h) = (p_w/p_h)^n(s_a/C_a). \qquad (10)$$

If we select as the distinguishing property of the transition temperature the fact that at it the finally saturated solutions of anhydride and hydrate respectively are identical, it follows that $p_a = p_h$ and therefore $C_h = s_h$ and $s_a = C_a$, which is the conclusion that has already been obtained in section (2). Also, since at this temperature $C_h/s_h = s_a/C_a = 1$, it follows that $P_h = p_a = p_h$, which expresses another general property of hydrates at their transition temperatures; as stated before, no molecular-kinetic explanation of this relation is known.

At temperatures other than that of transition the general fact that P_h is less than p_a or p_h below the transition temperature and greater above it can be used to determine which is the stable substance. For it follows from (10) that above the transition temperature, since P_h is greater than p_a or p_h, C_a is greater than s_a and s_h is greater than C_h, and therefore the anhydride is stable in the presence of its saturated solution. Similarly it can be shown that the hydrate is the stable substance below the transition temperature.

These conclusions from the thermodynamic relations agree completely with those already obtained from the solubility curves of the figure, which are based on the data for the solubility of milk-sugar. But the thermodynamic relations can give us further information which is not evident from the solubility curves. This is discussed in the two following sections.

4. A Method of Calculating the Solubility of Some Substances that Form Hydrates.

It is evident from (10) that

$$(p_a/P_h)^n = C_h/s_h, \tag{11}$$

and

$$(p_h/P_h)^n = s_a/C_a. \tag{12}$$

Since p_a, p_h, and P_h are usually measured with ease, these equations give a means of calculating the initial solubility of those substances for which C_h or C_a can be determined. For example, let the initial solubility of anhydrous milk-sugar at zero centigrade be calculated. Here $n = 1$, $C_a = 20$ millimols per 100 grams of water,[1] $P_h = 0.46$ cm. mercury nearly, since the saturated solution at zero is of 0.3 molal concentration and its vapor pressure is nearly the same as that of water, and I find P_h to have the values 43.3 at 90°, 7.2 at 60°, giving by extrapolation with the formula of Clausius, P_h at 0°, 0.062 cm. From these data s_a is calculated from (12) to be 148 millimols per 100 grams of water. By experiment I have found s_a to be 125. The agreement is as good as could be expected, considering the large possible error in the determination of P_h, which cannot be observed at 0° on account of the sluggishness of its establishment.

[1] Journal American Chemical Society, **26**, 1074 (1904).

It is noteworthy that in the experimental determination of the quantities from which s_a is calculated it is not necessary to isolate the anhydride. Only in the determination of P_h from a partially dehydrated sample of the hydrate is it needful to have the anhydride in the solid state and it is here mixed with hydrate in such an intimate manner that it cannot be described as isolated.

5. The Influence of Foreign Substances on the Solubility of Hydrates and Their Anhydrides.

If the free energy of the hydration reaction that is described in section (3) be calculated by a method which is a combination of those under (*b*) and (*c*), employing a reservoir of an unsaturated solution containing hydrate in concentration c_h and anhydride in concentration c_a and having a vapor pressure p_s, it is found that per mol of hydrate formed the energy is

$$W = nRT \log p_w/p_s + RT \log s_a/c_a + RT \log c_h/s_h. \qquad (13)$$

If this value is put equal to (7),

$$\frac{c_h}{c_a(p_s)^n} = \frac{s_h}{s_a(P_h)^n}, \qquad (14)$$

which is independent of the concentration.

As Nernst[1] has pointed out, since the vapor pressure of a dilute solution changes only very slightly with the concentration, equation (14) shows that the ratio of hydrate to anhydride is nearly constant in dilute solution, particularly if n is small. It is, however, to be expected that when n is large there will be an appreciable decrease of the ratio of hydrate to anhydride if the vapor pressure lessens. For example, if a chosen dilute aqueous solution at 20° contains a dekahydrate and its anhydride in equilibrium in the ratio $c_h/c_a = 1.50$, the addition of a foreign substance in tenth molal concentration would be expected to change the vapor pressure of the solution, according to Raoult's law, from 1.750 cm. mercury to 1.747 cm., which by (14) would change c_h/c_a from 1.50 to 1.47, an alteration of 2 per cent. Although the magnitude of such changes of hydration

[1] Loc. cit. Equation (14) differs from the similar one obtained by Nernst in the respect that the factors which compose Nernst's constant are here separated and identified with other physical quantities.

equilibrium is small, it is nevertheless sufficient, as I have shown at another place,[1] to account quantitatively for the lowered freezing temperatures of solutions, which are not inconsiderable depressions. I shall seek now to show that such changes of hydration equilibrium may also be the cause of well recognized regularities in the change of solubility of hydrates and anhydrides that occur when other, apparently indifferent, substances are present in the solution.

First, to determine the character of these regularities. I regard the best evidence on the change of solubility of hydrates to be that given by the experiments and the theory of Goldschmidt,[2] which he has summed up in the phrase "the molecular increase of solubility of hydrates."

These experiments give the solubility at room temperature of the bi- and tetra-hydrates of sodium paranitrophenolate in pure water and in molal solutions of urea, glycerine, acetone, propionitrile, acetonitrile, urethane and alcohol. It was found that all the solutions except the alcoholic dissolve more hydrate than does pure water, that the increase of solubility is nearly constant for the same hydrate in the different solutions, and that the ratio of increase of solubility of tetrahydrate to that of bihydrate is a constant 1.02.[3] The experiments of Löwenherz[4] also give evidence on the change of solubility of hydrates. He found that urea causes hardly a measurable change in the solubility of sodium sulphate dekahydrate, but a large decrease (13 per cent.) in the solubility of anhydrous sodium sulphate. To sum up then, it is found that the solubility of hydrates is frequently increased by foreign substances, never markedly decreased, and that the higher hydrate shows a greater increase of solubility than the lower.

The extensive evidence on the change of solubility of anhydrides has also been expressed in the form of a general regularity, namely, that the solubility of anhydrides is decreased by the presence of

[1] PHYSICAL REVIEW, **21**, 16 (1905).

[2] Zeitschrift für physikalische Chemie, **17**, 145 (1895).

[3] Goldschmidt has given a theory of this change of solubility, and from it has calculated this ratio to be 1.02, in full agreement with observation. For the details of this instructive theory, which in many respects is similar to the one here given although their initial assumptions are different, I refer to Goldschmidt's article.

[4] Zeitschrift für physikalische Chemie, **18**, 70 (1895).

foreign substances,[1] which in most of the experiments, have been salts.

It can be shown that these changes of solubility are to be expected from theoretical considerations, as follows: If a typical anhydrous substance A forms a series of hydrates in solution, its final solubility can be expressed as

$$S_a = s_a + C_{h_1} + C_{h_2} + C_{h_3} + C_{h_4} + \cdots$$

where the numerical subscripts denote the number of molecules of water in the hydrate. A relation of the form of (14) connects s_a and each C_h, and it is evident from (14) that the dissolution of a foreign substance in the solution and the accompanying decrease of vapor pressure of the solution will change the final solubility of A to

$$S_a' = s_a + C_{h_1}' + C_{h_2}' + C_{h_3}' + C_{h_4}' + \cdots$$

where each C_h' is less than the corresponding C_h, and S_a' therefore less than S_a. Thus there is to be expected a decrease in the solubility of anhydrous substances which form hydrates in solution caused by the presence of foreign substances in solution, a conclusion that agrees with the previously mentioned observed regularity of anhydrides.

The final solubility of a hydrate, H_3 for instance, in water can be expressed as

$$S_{h_3} = C_a'' + C_{h_1}'' + C_{h_2}'' + s_{h_3} + C_{h_4}'' + \cdots$$

and its solubility in a solution of a foreign substance

$$S_{h_3}' = C_a''' + C_{h_1}''' + C_{h_2}''' + s_{h_3} + C_{h_4}''' + \cdots$$

It is evident from (14) that the concentration of the anhydride and those of the hydrates of lower water content than H_3 are increased by the presence of the foreign substance, but that the concentrations of the hydrates higher than H_3 are decreased. Two effects therefore oppose each other and it is not clear whether the final solubility of the hydrate will be lessened or raised by the foreign substance. On the other hand if the solubility equations of a

[1] Rothmund, Zeitschrift für physikalische Chemie, **33**, 401 (1900). Rothmund has used the word "nonelectrolyte," but it is apparent that the substances whose solubility is decreased may be equally well classed as "anhydrides."

higher hydrate are expressed as has been done for H_3, it is evident that the number of substances whose concentration is increased is greater and the number whose concentration is decreased is less for the higher hydrate, and it is to be concluded therefore that at temperatures where the two hydrates give saturated solutions of nearly the same concentration, the higher hydrate will show a greater tendency to increase in solubility in a solution of a foreign substance. This conclusion is strictly applicable only to hydrates at their transition temperatures, because it is only at these temperatures where the two solutions are identical that the relative change of solubility of the two hydrates can be determined by the relative number alone of dissolved substances whose concentrations are increased or decreased by the foreign substance. The conclusion agrees with the previously mentioned experiments of Goldschmidt which show that foreign substances increase the solubility of a tetrahydrate to a greater extent than that of a bi-hydrate.

The theoretical conclusions regarding the influence of foreign substances on the solubility of hydrates and their anhydrides thus agree in a clear and natural manner with well-established and hitherto unexplained facts.

The solubility of many gases, oxygen, hydrogen, nitrogen, for example, is less in solutions than it is in pure water. As these gases are all anhydrous substances, it is possible that their decrease of solubility is due to their being markedly hydrated in solution. True, the solutions that have been examined are mostly electrically conducting salt solutions, in which complications are likely to occur, such as electrostriction,[1] which are here not considered at all. Nevertheless, most of the few experiments on solutions of non-electrolytes indicate in the same manner the formation of hydrates of these gases in solution.

6. Discontinuous Changes of Melting and Polymorphism.

The explanation of some of the peculiarities of the transition temperatures of hydrates that I have attempted assumes that the substance that is unstable in the solid state is nevertheless stable in

[1] Drude and Nernst, Zeitschrift für physikalische Chemie, 15, 79 (1894). Nernst, Theoretische Chemie, 1900, 445.

solution, and that the formation of hydrate or anhydride which takes place discontinuously in the solid state at one temperature and pressure occurs in solution over a wide range of temperature and pressure. The discontinuity of such transition reactions as opposed to the continuous formation of most substances over a range of temperature, as, for example, the production of hydriodic acid from its elements, is so often emphasized that it seems to me important to understand that the discontinuity of the chemical change does not follow as a consequence of the discontinuity of the formation of the phases. The only reactions that take place at one temperature only are the transition reactions and the meltings. I have here endeavored to show that the transition of hydrates, and what is true of these transitions is quite applicable to all transitions, are not discontinuous in solution, and at another place[1] I have shown that the melting phenomena can also be clearly and quantitatively accounted for on the hypothesis that the solid exists dissolved in the liquid, like any ordinary solution, over a wide range of temperature, or, in other words, that the chemical reaction which gives rise under appropriate conditions of temperature and pressure to the phenomena of melting is quite similar to the ordinary balanced chemical reactions and are like these continuous, though some of its effects appear discontinuous. There is no example, as far as I know, of a chemical reaction which occurs at one temperature only.

8. SUMMARY.

The contents of this article may be summarized as follows:

The initial and final solubility curves for anhydrous and hydrated milk-sugar give an instructive view of the relations that cause the transition temperatures of hydrates. This theory, in which the two substances are regarded as present in equilibrium in solution over a wide range of temperature, shows how it is that the stable form has the smaller solubility and that there is no discontinuity in the properties of the solution at the transition temperature.

A thermodynamic theory of a typical hydration reaction is worked out, which expresses the relations of concentration and solubility that give rise to transition temperatures, leads to a method of cal-

[1] PHYSICAL REVIEW, l. c.

culating solubilities which is found to give an accurate value for milk-sugar, and forms the basis of an extension of Goldschmidt's theory of the influence of foreign substances on the solubility of hydrates.

Evidence is given that the discontinuous physical changes of state such as melting and transition, are the results of chemical changes (*i. e.*, the formation of new molecules) which are themselves continuous over a wide range of temperature.

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EVERY-DAY PROBLEMS OF THE MOVING COIL GALVANOMETER.

BY WALTER P. WHITE.

ALL moving coil galvanometers, when critically damped by the coil alone, are, for small deflections, equally effective in utilizing the energy of the source of current[1]; their efficiency as galvanometers depends on the deflection obtained with a given amount of energy, and therefore on the smallness of the controlling force. The work done by twisting the suspending wire during deflection bears a constant ratio to that expended during the same time[2] in heating the circuit with the coil at rest; that is,

$$\tfrac{1}{2}\vartheta^2 Q = .157\ I^2 R T. \qquad (17)$$

This energy equation,[3] by a change to practical units, becomes

[1] W. P. White, Sensitive Moving Coil Galvanometers, PHYS. REV., 19, 304, 1905.

[2] With a critically damped galvanometer 99 per cent. of the deflection is executed in the periodic time T. Hence this time may often be taken as the time the observer must wait to get his reading, and the time in which the current energy is expended. .999 of the deflection is completed in the time 1.5 T.

[3] The notation and the numbering of the equations are here consistent with the former article, *e. g.*:

Let K be the moment of inertia.
Q, the moment of torsion of the controlling force.
I, the current in microamperes.
θ, the angular deflection in two-thousandths of a radian.
R, the resistance of the whole circuit in ohms.
R', the the resistance of the coil.
H, the mean effective field strength.
l, the length of the vertical wire in the coil.
r, half the width of the coil.
$G, = Hlr$, the dynamic constant.
T, the undamped period.
$D', = G^2/R$, the damping coefficient of the coil.
$D, = 2\sqrt{KQ}$, the total damping coefficient necessary for critical damping.
$S, = \theta/I$, the current sensibility in megohms.
$V, = S/R$, the corresponding voltage sensibility.
Equation (17), alone, is in absolute units.

identical with the sensibility equation,

$$S^2 = 12.6 \frac{RT}{Q}. \qquad (11)^1$$

In the slightly different form :

$$V^2 R \frac{1}{T} = \frac{12.6}{Q} \qquad (18a)$$

the energy equation shows immediately, on the right hand side, the actual efficiency of the galvanometer; and suggests more directly the general problem of galvanometer work, which is to make the best possible combination of *all three* factors in the left hand member. The deflection for a given amount of energy and the normal-sensibility are each proportional to the square root of the second member. R is here the critical resistance.

The Second Condition. — This is expressed by the familiar equation

$$4\pi^2 K = T^2 Q. \qquad (1)$$

Combining the last two equations, we get

$$V^2 R \frac{1}{T^3} = \frac{\cdot 32}{K} \qquad (19a)$$

which is more convenient than (18*a*) when T is varied without changing K; that is, by varying the stiffness of the suspending wire.

Light Coils. — In this latter case, inspection of the equation shows that for an increase of period the sensibility increases still more rapidly, nearly as much, in fact, as in the same adjustment with galvanometers of the Kelvin type.[2] The advantage, then, of lengthening the period by reducing the stiffness of the suspension is relatively great. In the case (equation 18*a*) where the coil is enlarged, the sensibility only increases as the square root of the period. Reducing the suspension increases the efficiency of the galvanometer,

[1] Jaeger was apparently the first to give simple equations of this form. Zeitsch. fur Instrumentenkunde, 23, 261, 1903. Many important questions relating to the moving coil galvanometer are discussed in this article.

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as well as the period. Increasing the moment of inertia of the coil leaves the efficiency unaltered and merely increases the sensibility at the expense of a disproportionately protracted period. There is, therefore, nearly always a decided advantage to the user of a galvanometer in making the coil small. The only exception is where high sensibility is indispensable, and (after the suspension has been reduced to its smallest value) must be secured by greatly increasing both the size of coil and the period. In all other cases a heavy coil causes an unnecessary waste of time. If the suspension has at the same time its minimum value, the disadvantage of the increased period is partly offset by greater sensibility, though this is seldom worth what it costs; if both coil and suspension are heavy, there is practically no compensating advantage.

K has been made as small as .03 c.g.s. units without difficulty (see other article, p. 316), and a value of .05 units would, therefore, seem often attainable. Larger values for K are needed where the critical resistance is high (see p. 385 below). The smallest value of K of which I have been able to learn in a commercial instrument is .25 c.g.s. units, and some firms advertise instruments whose smallest value of K is over 1.5 units. Suspensions can readily be purchased giving a value of Q as small as .18 c.g.s. units.

The Third Condition, and the Magnet Strength. — A further limiting condition is found in the requirement of critical coil damping. A convenient statement of this condition for the moving coil galvanometer is obtained by combining equations (13) and (16), which gives

$$H = A\sqrt{\frac{R}{R'T}} \qquad (20a)$$

where A, nominally a constant, varies slightly with the inert material in the coil, which was neglected in setting up the original equations. Postponing for a moment the consideration of its variations, we reach the following results:

(1) The sensibility is not directly dependent upon the field strength. In general, an unduly weak field will not prevent a galvanometer from being made sensitive.

(2) The period, however, except for the somewhat limited variations possible in the ratio R/R', depends almost entirely upon the field strength. The shortness of period possible with a light coil requires also a strong magnet. Weak magnets tend to make galvanometer work unnecessarily tedious.

(3) A high external resistance increases the difficulty of securing a short period, and may demand an increase in the field strength.

(4) If the internal resistance is increased, the field strength may, other things being equal, be diminished, and conversely. These two quantities are therefore to a certain extent substitutes for each other. An increase in the coil resistance, however, often reduces the sensibility undesirably. It is least detrimental where most needed, that is, when the external resistance is high. Another obstacle to an increase of R', however, is set by the size of the coil. The physical interpretation of the value of R' in this connection is, of course, that R' serves as a measure of the number of turns of wire in the coil. To increase it with a given coil demands the use of finer wire, and when the limit of fineness is reached, any further increase necessitates making the coil heavier. The most sensitive galvanometers, therefore, that is, those with the smallest coils, will require the strongest fields, and this requirement will be greater the shorter the period and the higher the external resistance.

By the method used in getting equation (16) it can be shown that the largest value of R' is, to a rather rough approximation, $680\ K/r_2$ if the finest available wire is $1\frac{1}{2}$ mils in diameter.

For A equal to 750, a fair average value, Table I. shows the field strength necessary to give different periods when the resistance of the coil is $\frac{1}{4}$, and 1, 2 and 3 times that of the external circuit, that is, for $R/R' = 8,\ 2,\ \frac{8}{3}$ and $\frac{4}{3}$.

TABLE I.

Approximate field strength required to give different periods for various ratios of coil and total resistance.

T	$\frac{R}{R'} = 8$	$\frac{R}{R'} = 2$	$\frac{R}{R'} = \frac{8}{3}$	$\frac{R}{R'} = \frac{4}{3}$
1 second.	2106 lines.	1053	920	870
2 "	1500 "	750	650	613
3 "	1220 "	610	530	500
4 "	1050 "	525	460	433
8 "	750 "	375	325	308

In a number of galvanometers of American manufacture, H varied from 200 to 600 lines.

Zero Shift.—The fear of the detrimental magnetic effect is sometimes given as a reason for employing the weak magnets often favored by instrument-makers. Equation 20 leads to a convenient statement of the conditions governing this effect. The magnetic attraction has been shown (page 314, of the former article) to be, for a given per cent. of magnetic impurity, proportional to the square of the field strength, and to the mass of the coil, regardless of its shape or dimensions. The detrimental effect on the readings is proportional to this quantity divided by the controlling force; that is, if M is the detrimental effect, and changes in the form of the coil are excluded,[1]

$$M \propto \frac{H^2K}{Q}, \text{ or } M \propto H^2T^2. \tag{21}$$

By combination with equation (20) we get, for critical coil damping,

$$M \propto TA^2\frac{R}{R'}. \tag{22}$$

Increase in field strength, therefore, when used to shorten the period, so far from increasing, diminishes the detrimental effect.

The magnetic effect is detrimental in two ways. First, it tends to keep the coil in a fixed position, and hence increases the controlling force. This of course does very little harm except where maximum galvanometer efficiency, and, therefore, the minimum value of the controlling force, is required. The second effect, of far less magnitude, is in general much more important, namely, the shifting of the zero after deflection, which results from a slight change in the direction of magnetization of the coil.

The importance, in this particular connection, of magnet strength can easily be exaggerated. The detrimental effect is generally chargeable to the coil. With reasonably good coils, it is troublesome only in the strongest fields and should not be perceptible with magnets of ordinary strength. For instance, in a Leeds and Northrup H-form galvanometer, with cast-iron magnet and open field of 420

[1] M is of course less for the same K as the coil becomes wider. See page 315 of the former article.

lines,[1] the zero shift could not be detected, that is, it was certainly less than .01 per cent. The same was true of a Siemens & Halske galvanometer, with a radial field of about 1,300 lines and 8-second period.[2] The control was here increased more than 30 per cent. On the other hand, in a galvanometer of a type much advertised in the nineties, where the coil and suspending wires were enclosed in tubes, a magnet built up of small steel horseshoes, presumably to secure special field strength, barely gave 200 lines. The coil weighed 16 grams and required an auxiliary damper to bring it to rest in 24 seconds. After an excessive deflection the spot of light usually took an appreciable fraction of an hour to get back to the scale at all, so great was the zero shift. The fact that this instrument is less than seven years old shows what gratifying progress has recently been made in galvanometer construction. It is still true, however, that except where extreme sensibility is needed, the periods of many instruments are too long and the magnets too weak. The case of the H-form cast-iron magnet just mentioned, whose field gave very large clearance for the coil and was not especially uniform, shows that the detrimental magnetic effect need not be serious for fields of a thousand lines, and therefore the field of a first-class galvanometer should not be less than this, except where the period is such as to render a weaker magnet actually desirable.

A moving coil galvanometer consists essentially of a magnet, a coil, and a suspending wire. If the period is long, all difficulty in constructing either coil or magnet disappears. The value of the instrument then depends mainly on the suspension, and therefore, for the most part, on the wire manufacturer, and not the instrument-maker. The galvanometers of ten years ago are therefore fairly sensitive, and, were it not for their remarkably weak fields, would in this respect nearly equal the best to-day. When the period is

[1] The coil was made in this laboratory from wire furnished by the Leeds and Northrup Company. In winding the coil, the most scrupulous cleanliness was observed in every respect and the work was done in a room far removed from the machine-shop.

Dust and dirt, which nearly always contain traces of iron, are known to be fatal to the magnetic purity of galvanometer coils. It is important to note that an excellent coil may be ruined by a very slight amount of careless handling or a few minutes' exposure to a dusty atmosphere.

[2] The suspension was as usual by phosphor-bronze ribbon. This case proves that the set of fine phosphor-bronze suspensions need not cause appreciable zero shift.

short, however, the magnet must be strong, and if the sensitiveness is at the same time to be great, the coil must be small as well. Normal-sensitiveness combined with shortness of period is therefore the real test of the instrument-maker's skill, as it is also the measure of general usefulness, except for ballistic work. If the critical resistance is also high, the test is especially severe.

GALVANOMETER POSSIBILITIES.

The following table gives the sensibility attained and the coil resistance needed for various periods and resistances, computed by means of some of the equations given above. The field strength is taken at 1,000 lines, and easily attainable values for Q and K are assumed. The table therefore does not attempt to represent the extreme possibilities of galvanometer construction.

TABLE II.

Typical galvanometer performance.
Field strength, 1,000 *lines. Minimum value of* Q, .17; *of* K, .05.

Moment of torsion, Q.	.17		.17		.495		1.98	
Moment of inertia, K.	.43		.05		.05		.05	
Period, T.	10		3.4		2		1	
Resistance, R.	50	500	50	500	50	500	50	500
Voltage sensibility, V.	3.8	1.2	2.2	.71	1.0	.32	.36	.11
Current sensibility, S.	192	610	112	350	50	160	18	57
Coil resistance, R'.	3	30	8	82	14	140[1]	28	280[1]

In practice, the effective sensibility can be made greater than here given by increasing the scale distance. In the table, the loss in sensibility when the period is decreased from 10 to 3.4 seconds is only about .3 as much as in the further reduction from 3.4 seconds to 1. This is because the first change is produced by altering the moment of inertia, K, while the second involves an increase in the moment of torsion, Q. It is always more profitable in point of sensibility to decrease the period by decreasing K than by increas-

[1] These values are impossible, since when K is .05 the resistance of an open coil cannot easily be made greater than 100 ohms. The above combinations, therefore, of high resistance and short period require either a stronger field or else an increase in both K and Q, with resulting loss of sensibility. On the other hand, for the 10-second period a weaker field would evidently suffice.

ing Q. The table in this case illustrates the discussion on page 383, above.

Auxiliary Damping. — When an auxiliary damper of any kind is added to the coil, the current energy is divided between the main circuit and this damper in proportion to their damping coefficients. If D' is the damping coefficient of the main circuit, d of the frame, and $D = D' + d, = 2\sqrt{KQ}$, the critical damping coefficient, equations (18*a*) and (19*a*) become

$$V^2RQ\frac{1}{T} = 12.6\,\frac{D'}{D} \qquad (18b)$$

$$V^2RK\frac{1}{T^3} = .32\,\frac{D'}{D} \qquad (19b)$$

Equation (20*b*) may be treated as follows:

For critical damping $2\sqrt{Q(K+k)} = D' + d$,

or

$$\frac{4\pi(K+k)}{T} = \frac{G^2}{R} + \frac{g^2}{r'} \qquad (23)$$

where the small letters apply to the frame.

Hence

$$\frac{K+k}{T} = H^2\frac{R'}{R}\frac{K}{A^2} + \frac{H^2}{a^2}\frac{r'}{r'}k = H^2\left(\frac{R'}{R}\frac{K}{A^2} + \frac{k}{a^2}\right)$$

$$= H^2\frac{R'}{RA^2}\left(K + k\frac{A^2}{a^2}\frac{R}{R'}\right). \qquad (24)$$

But

$$\frac{D'}{d} = \frac{\frac{G^2}{R}}{\frac{g^2}{r'}} = \frac{\frac{H^2R'K}{A^2R}}{\frac{H^2r'k}{a^2r'}} = \frac{K}{k}\frac{R'}{R}\frac{a^2}{A^2}$$

(24) thus becomes:

$$\frac{1}{T} = \frac{H^2R'}{RA^2}\left\{\frac{K + \frac{d}{D'}K}{K + K\frac{d}{D'}\frac{R'}{R}\frac{a^2}{A^2}}\right\} = \frac{H^2}{A^2}\frac{R'}{R}\left\{\frac{D' + d}{D' + \frac{R'}{R}\frac{a^2}{A^2}d}\right\},$$

whence

$$H = A\sqrt{\frac{R}{R'T}}\sqrt{\frac{D' + d\frac{R'}{R}\frac{a^2}{A^2}}{D' + d}}. \qquad (20b)$$

$$\frac{a^2}{A^2} = \frac{1}{n}$$

approximately, unless K' is large.

Since there is always some air damping, equations (18*b*) and (19*b*) should in strictness be used instead of (18*a*) and (19*a*), but for practical purposes this is seldom necessary.

The loss in sensibility from energy wasted in dampers is in general not serious. Even when the circuit furnishes only one-fourth of the damping, the sensibility is still half the maximum. On the other hand, the auxiliary damping does not alter with the external resistance, so that in work where changes in the circuit resistance are necessarily frequent a large amount of auxiliary damping may yield an advantage far outweighing the loss in sensibility which it entails. The galvanometer with auxiliary damper will also come to rest on open circuit, which is often a great convenience. If, however, constant galvanometer sensibility is needed, constant resistance must be provided for, and in that case the auxiliary damper loses its main advantage.

With an auxiliary damper and critical damping the period may be made somewhat shorter for the same magnet strength than where the coil is damped wholly by the circuit. This gain is due merely to the fact that the value of $A\sqrt{R}/R'$ is less for the damping frame than for the coil. The resulting period has therefore a lower limit in the period characteristic of the frame alone, and cannot even be brought very near that limit unless the amount of auxiliary damping is large.

The actual shortening in period increases with the amount of damping and with R/R'. With R/R' very large, it is proportional to D/D'. For air or oil damping the same figures can be approached, even when R/R' is not very large.

Galvanometer Calculations. — On account of the simplicity of the principal equations, the purchaser or occasional user of a galvanometer may readily secure the advantages of computation in adapt-

ing his instruments to their work. Equations (18*a*), (1) and (20) can obviously be worked backward, that is, from the published or observed values of sensibility, period, etc., the fundamental constants

$$Q,\ K,\ \frac{H\sqrt{R'}}{A}$$

are easily found. With a knowledge of the possibilities of the instrument as determined by the values of these three constants, the best obtainable combination of sensibility, period and resistance can be decided upon.

The Measurement of Field Strength. — By means of equation (20), the field strength of a galvanometer can be found by measurements of time and resistance alone; that is, without knowing the size of wire in the coil, the number of turns or the moment of inertia; indeed, without touching the coil at all. For this purpose it is well to know the value of A more accurately. To attain this result, equation (16) may be rederived, taking account of the dead wire and other inert material in the coil. l is the vertical wire in the coil. Let h be the total length of vertical wire actually passing through the field, and b, the total length of horizontal wire. Let K' be the moment of inertia of the mirror and other coil fittings. Let w be the product of the resistance per unit length of the bare wire by the mass per unit length, m. This is constant for any material, and for copper equals .0000145. Let n be the ratio of the insulated and varnished wire to the bare wire. Then

$$^1G = Hhr;\quad K = nm\left(l + \frac{b}{3}\right)r^2 + K' \qquad R' = \frac{(l+b)w}{m}.$$

Eliminating m and r

$$G^2 = \frac{H^2R'}{w}\,\frac{h^2}{(l+b)(l+b/3)}\,\frac{K-K'}{n}. \tag{25}$$

Eliminating G^2 by (13) and (5), and Q by (1), and giving w its numerical value for copper, we get:

$$H = 425\sqrt{\frac{(l+b)(l+b/3)}{h^2}}\,n\,\frac{1}{1-K/K'}\sqrt{\frac{R}{R'T}} \tag{20c}$$

whence

$$A = 425\sqrt{\frac{(l+b)(l+b/3)}{h^2}}\,n\,\frac{1}{1-K'/K}$$

[1] These values rather than the simplified ones should be used in designing coils.

A is thus the product of four factors; one is constant, the other three enter by their square roots, so that any uncertainty in their values has only half its proportional effect on the result. The second factor depends on the dimensions of the coil and field, and can be easily calculated. It will, moreover, be practically constant for the same instrument, and will seldom vary over 20 per cent. K'/K will be small, and K' can be estimated from the dimensions and known density of the coil fittings, which will usually be of brass or glass. The second factor, n, is more uncertain. It will ordinarily vary from 1.4 to 1.6, and will be somewhat less for larger sizes of wire. In a coil 2×5 cm., wound with 2 mil. wire (.005 cm. diameter) A was approximately 750. Sixty-two per cent. of the wire passed through the field. In general, A will vary between 600 and 800, depending mainly on the width of the coil, and with coils of the usual dimensions it will vary approximately 10 per cent. for a change of 50 per cent. in coil width. The error in determining field strength by application of equation (20*b*) will seldom exceed 10 per cent.

Adjustments. — When a galvanometer is to be used for any length of time on one piece of work, an hour or so is usually well spent in adjusting it for the most effective service. In such cases a convenient procedure is as follows: The instrument is set up, with all damping frames removed, in series with a resistance box and connected to a suitable source of electromotive force, such as a potentiometer. The critical resistance and the corresponding sensibility are then determined. This can be done within 2 or 3 per cent., since a resistance which is 10 per cent. too great or too small produces a noticeable effect upon the damping. The internal resistance is also found, and hence, approximately, that of the coil. The period is also observed. The data thus obtained determine completely the possibilities of the instrument; the most satisfactory adjustment can readily be computed and made in the quickest way. For this the following equations may be used:

$$T^2 \propto \frac{K}{Q}$$

$$V \propto \frac{G}{QR} = \frac{H/r}{QR} \qquad (26)$$

$G^4 \propto R^2QK$, for critical damping.

If we regard the coil as a fixed part of the instrument, the changes which can be made, in the order of their ease, are:

1. The total resistance, R, can be altered.

2. The field strength, H, can be decreased, if the instrument is provided with a magnetic shunt.

3. The moment of inertia, K, can usually be increased by hanging a mass from the coil.

4. A damping frame can usually be attached to the coil.

5. The moment of torsion, Q, of the suspending wire can be altered, by substituting a new wire or by shortening the one in place.

Any single change will of course spoil the adjustment for critical damping, hence at least two changes must be made for any new adjustment.

The above changes permit the following adjustments:

1. It is desirable to increase the resistance R, N times.

Compensating Change.	Change in V.	Change in T.
(a) add a damper.	dim. N times.	increases.
(b) dim. Q N^2 times.	inc. N times.	increases N times.
(ab) dim. Q N times, add damper.	none.	increases.

2. The sensibility, V, is to be increased N times.

Changes to effect this.		Change in T.
(b) dim. Q N^2 times.	Inc. R N times.	Increases N times
(c) dim. R N times.	Inc. K N^2 times.	Increases N times.
(bc) dim. Q N times.	Inc. K N times.	Increases N times.
(d) dim. R N^2 times.	Dim. H N times.	no change.

3. The period, T, is to be increased N times.

Changes to effect this.		Change in V.
(e) inc. Q N^2 times.	dim. R N times.	diminishes N times.
(f) inc. Q N^2 times.	add a damper.	diminishes N^2 times.

Notes.

(a) The increase of period will be due to the weight of the damper and its amount will depend on the amount of change to be made; that is, on the value of N, and also on the value of R/R'. A large value of R/R' and a small value of N are the conditions most advantageous for the damper. See equation ($26\,b$).

(ab) Any other desired combinations of a and b can of course be made as readily as this particular one. In general, adjustments involving a change in Q are not likely to come exactly right the

first time. It will usually be preferable to make the final and more exact adjustment, where this is needed, in some other way, as, for instance, to alter the scale distance in order to change slightly the effective sensibility.

(f) On account of the weight of the damper, the decrease in the period is less than with (e). The method in (f) would be preferable where the resistance could not be diminished.

A damping frame can usually be adjusted by trial about as quickly as by calculation.

It is of course possible to decrease the period and increase the sensibility at the same time by making a large decrease in the resistance, but the resulting gain is so small as seldom to be worth while.

Ballistic Efficiency. — The advantages for ballistic work of a damped galvanometer, and therefore of the moving coil galvanometer, are sufficiently well known.[1] If S_B is the ballistic sensibility (in scale divisions per microcoulomb),

$$S_B = S\frac{2\pi}{TX} \qquad (27)$$

where X depends upon the damping, and for critical damping equals e, the Napierian base. This equation involves, as usual, the assumption that the discharge passes before the coil has had time to move appreciably. In many cases the error due to this assumption is not negligible, and a correction for the time of discharge is applied.[2]

Equation 27 indicates that for closed circuit work the best construction for the ballistic galvanometer is ordinarily the same as for the constant current galvanometer of equal period. The period of the ballistic galvanometer, however, must in general be longer than with the direct current instrument, to permit of accurate reading. When the deflection occurs on open circuit, as in discharging condensers, there is no coil damping, and the sensibility can without inconvenience be increased very considerably by using a strong field. A high resistance may then be inserted, sufficient

[1] H. Diesselhorst, Drud. Ann., 9, 458, 1902. O. M. Stewart, PHYS. REV., 16, 158, 1903.

[2] E. Dorn, Wied. Ann., 17, 654, 1882; H. Diesselhorst, Drud. Ann., 9, 712, 1903; F. Kohlrausch, Lehrb. der Prak. Phys., 10th ed., p. 480.

to give critical damping if the coil is brought to rest by closing the circuit. A galvanometer thus made sensitive may therefore be treated as a critically damped instrument of very high resistance.

The sensibility of a critically damped ballistic galvanometer, for the same control, can also be increased in another way, which applies to both closed and open circuits, namely, by diminishing the period. The ballistic, unlike the steady current galvanometer, does not when critically damped utilize any definite fraction of the available electrical energy. The physical reason for this is found in the fact that the energy taken up by the coil depends in part upon the distance it rotates while the impulse is acting upon it, and this distance obviously increases as the coil becomes smaller.

The sensibility cannot be increased indefinitely by either of these methods, since that would involve getting an infinite amount of work from a finite amount of energy. When the field strength of the steady current moving coil galvanometer is indefinitely increased, the sensibility also increases and with it the energy stored up during deflection; but the instrument becomes overdamped; that is, it demands a longer time and therefore more electrical energy, in order to produce that deflection. With the ballistic galvanometer the energy cannot be increased, and therefore the deflection must ultimately reach a limit, no matter how short the period or how strong the field. How this limit occurs can perhaps be best seen by finding an expression for the energy. The total electrical energy, in absolute units, equals

$$\frac{1}{R}\int_0^\tau E^2 dt = \frac{E_1^2\tau}{R}$$

where E is the instantaneous E.M.F. and τ, the duration of the impulsive discharge.

The energy taken up by the coil may be found as follows: Assuming that τ is very small — the assumption involved in equation 27 — the velocity of the coil at the end of the impulsive discharge is:

$$\frac{G\int_0^\tau E dt}{RK}, \quad = \frac{GE_2\tau}{RK}.$$

The energy is: $G^2E_2^2\tau^2/2R^2K$.

Putting in, for simplicity, the condition of critical damping, $G^2/2R = \sqrt{KQ}$, this becomes:

$$\frac{E_2^2\tau^2}{R}\sqrt{\frac{Q}{K}} = \frac{E_2^2}{R}\frac{2\pi\tau^2}{T}.$$

The fraction of the total energy taken up by the coil is therefore:

$$\frac{\frac{E_2^2}{R}\frac{2\pi\tau^2}{T}}{\frac{E_1^2\tau}{R}} = \frac{E_2^2}{E_1^2}\frac{2\pi\tau}{T}.$$

E_2^2/E_1^2 will vary from ½ to 1, depending on the wave form of the impulsive discharge. If τ/T is small, the critically damped ballistic galvanometer is very inefficient, and its sensibility can be increased without difficulty, by diminishing its period or otherwise. This is, of course, the usual case. As τ/T increases, the instrument will use a larger fraction of the available electrical energy. In this case, therefore, the deflection will approach its limit for a given value of Q; but in this case, also, the fundamental assumption of equation 27 no longer holds, and the correction for the time of discharge increases. It is the increase of this correction as T grows smaller which furnishes the needed limiting condition to the increase of sensibility.

With a condenser discharge the case is slightly different, for there the discharge itself is also protracted by the reaction of the moving coil.

Summary and Conclusions.

I. All galvanometers when critically damped by the coil alone are subject to three conditions.

The first of these is that the galvanometer during deflection utilizes nearly 16 per cent. of the energy of the steady current, I^2RT. The second is the well known relation between moment of inertia, moment of torsion and periodic time. These conditions lead to the familiar relations between sensibility, period, resistance and controlling force.

The third is the well-known condition for critical damping. For the moving coil galvanometer this condition may be expressed

in a new and convenient form as a relation between the periodic time and the field strength, modified by the ratio between external and internal resistance, and also to a slight extent by the form of coil. The period, therefore, is practically determined by the field strength, no matter what the sensibility may be.

II. To the three generally recognized points of excellence in moving coil galvanometers it therefore seems desirable to add a fourth. The four points then are:

1. *Steadiness of the Coil.* — This depends upon accuracy of construction, but more upon the conditions under which the instrument is used.

2. *Smallness of Controlling Force.* — This depends upon delicacy of construction. It is an advantage which may be variously used to secure large sensibility, high resistance, or shortness of period.

3. *Ability to Secure Short Period.* — This depends essentially upon field strength. Whether a short period is consistent with a given sensibility, etc., depends upon the delicacy of construction. The question here is of the ability to secure the short period at all in a critically damped instrument.

4. *Constancy of Zero.* — This is wholly a question of magnetic action. It depends upon the shape of the field and the width and magnetic purity of the coil. It also increases as the period becomes shorter and the coil resistance greater.

III. The advantages of light coils are often insufficiently appreciated.

IV. High normal-sensibility, combined with shortness of period, is the real test of skill in galvanometer construction.

V. A high total (critical) resistance increases the difficulty of securing these advantages.

VI. Auxiliary dampers diminish sensibility, but have certain obvious advantages. Under some conditions they diminish the possible period more than they do the sensibility. This action may be greater with air and oil than with magnetic dampers.

VII. It is possible to determine within 10 per cent. the field strength of a galvanometer by measurements of time, sensibility and resistance, combined with inspection of the coil.

VIII. Nearly all that is practically important in the theory of moving coil galvanometers can be included in three short equations between quantities which can easily be determined for most instruments. Computation, therefore, can be easily and advantageously employed in adapting a galvanometer to any particular task.

IX. The ballistic galvanometer, as usually employed, with an impulsive discharge of very short duration, is very inefficient. The quantity of electricity required to produce a given deflection is of the same order of magnitude as with the steady current instrument, but the energy is far greater. As the time of the discharge approaches the periodic time of the galvanometer, the efficiency increases.

GEOPHYSICAL LABORATORY,
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WASHINGTON, D.C., May 29, 1906.

ON PRECISION MEASUREMENTS WITH THE MOVING COIL BALLISTIC GALVANOMETER.

By Anthony Zeleny.

THE moving coil ballistic galvanometer possesses an important advantage over the stationary coil type in that it is free from ordinary external magnetic disturbances, but it presents a number of difficulties for work of high precision. It is the object of this paper to show how these difficulties may be overcome so that measurements with this galvanometer can be made to as high a degree of accuracy as is attainable with direct deflection methods. The various details, many of which are well known and are included only for the purpose of completeness, will be considered under the following subdivisions.

§ 1. Set in the fiber, hysteresis, and zero or null point readings.
  (*a*) In ballistic work.
  (*b*) With continuous currents.
  (*c*) Choice of suspension fiber.
§ 2. Damping on closed circuit.
§ 3. Adjustment for equal deflections. Circular scale. Increase of period. Shunting of galvanometer.
§ 4. Methods of bringing the coil to rest.
  (*a*) In open circuit work.
  (*b*) In closed circuit work.
§ 5. Throws from a vibrating coil.
§ 6. The variation of the constant. The damping factor.
§ 7. Methods of determining the constant.
  (*a*) The figure of merit and period of vibration method.
  (*b*) The earth inductor method.
  (*c*) The standard solenoid method.
  (*d*) The standard condenser method.
§ 8. The standard mutual inductance coil.

§ 9. Correction for thermo-electric currents.
(*a*) Changing from closed to open circuit.
(*b*) Changing from open to closed circuit.
§ 10. Galvanometer resistance by a method of damping.
§ 11. Conclusion.

§1. SET IN THE FIBER, "HYSTERESIS," AND ZERO OR NULL POINT READINGS.

When a set is "given to a fiber" during an observation, so that the coil does not return to its original position, the error due to it may be avoided in the following manner:

(*a*) *In Ballistic Work.* — A throw that is at least equal to the maximum to be used is given to the coil, so that a set is affected in the direction of the throws which are to follow. The coil on returning to the null point must not be allowed to move past it (see §4), as otherwise a part of the set is removed.[1] Subsequent throws in the same direction cause little or no additional set. It rarely happens that an additional set is given, and if any is observed the throw producing it must be discarded.

(*b*) *With Continuous Currents.* — The correction for the set is avoided in the same way as in ballistic work. To note the amount of the set the coil must here also be brought aperiodically to the null point. The null reading observed after the deflection and not the original one, if it differs from it, must be employed in the calculation of the deflection.

In comparing currents which are not of approximately the same strength regard must be taken for an apparent "hysteresis" which exists in many if not all moving coil galvanometers. The same current produces a different deflection depending on whether it has increased from zero or decreased from a larger value. The observations of Table I. indicate the amount of this variation in the case of two galvanometers. The null point after the larger reading remained the same as that after the lesser one in each case. Dif-

[1] In most galvanometers the coil can move beyond the null point an amount equivalent to two or three centimeters on the scale without producing an appreciable effect on the set or the magnetic hysteresis of the coil.

ferent currents were used in the three cases given, so as to make the deflections in all of them about the same.

TABLE I.

Galvanometer.	Suspension.	Deflection in Cm. Current Increased from Null Reading.	Deflection in Cm. Current Decreased from Twice Its Value.	Variation.
An open coil type. (Leeds & Northrup "H" Type.)	Phosphor-bronze.	10.91	11.00	0.8 %
	Steel.	12.64	12.69	0.4 %
A cylindrical coil type. (Made in the laboratory. Coil of special "iron free" wire on wooden spool.)	Phosphor-bronze.	10.42	10.68	2.0 %

These variations are not due to changes produced by the larger current heating the fiber, for the deflection taken again from the null position is the same as it was in the first case. They are probably due to changes in the direction of magnetization of the magnetic impurities within the coil.

Whatever may be the cause of this hysteresis observed when employing continuous currents, it is probable that ballistic throws of unequal magnitude are not proportionally affected by it. This hysteresis even affects throws of equal magnitude. After some period of rest the first throw differs from the following ones obtained for the same quantity by an amount usually exceeding 0.2 per cent. and therefore should always be discarded.

(*c*) *Choice of Suspension Fiber.* — It is desirable to choose the suspension fiber[1] which gives the least amount of set after reversal of deflection. A phosphor-bronze strip that gives a set of several millimeters can often be replaced by a phospor-bronze wire, a coarser strip or a steel fiber giving much less set. In each case, however, this is accomplished at the expense of sensitiveness, as shown in Table II., so that in many cases the 1.5 mil phosphor-bronze strip is selected. In the observations given in Table II., the

[1] W. E. Ayrton, Phil. Mag., 1890, Vol. 30. p. 58; Electrical World, 1892, Vol. 19, p. 178.

lower suspension was the same phosphor-bronze spiral in each case, the upper suspension only being changed.

TABLE II.

Upper Suspensions of Equal Length.	Sensibility in "Megohms."	Time of Double Vibration on Open Circuit.	Ballistic Throw for Equal Quantities.	Set in Fiber on Reversal After Full Scale Deflection of 25 Cm. = 14°.
1.5 mil phosphor-bronze strip.	252.0	17.88 sec.	9.03 cm.	0.27 cm.
1.5 mil phosphor-bronze wire.	109.6	12.00 "	5.80 "	0.06 "
3 mil phosphor-bronze strip.	47.8	7.80 "	3.77 "	0.04 "
A steel strip.	23.1	5.44 "	2.60 "	0.00 "

§ 2. DAMPING ON CLOSED CIRCUIT.

The value of the damping factor on open circuit is usually about 1.02, but on closed circuit it is greatly increased and so diminishes[1] the sensitiveness of the galvanometer. Fig. 1 gives an experi-

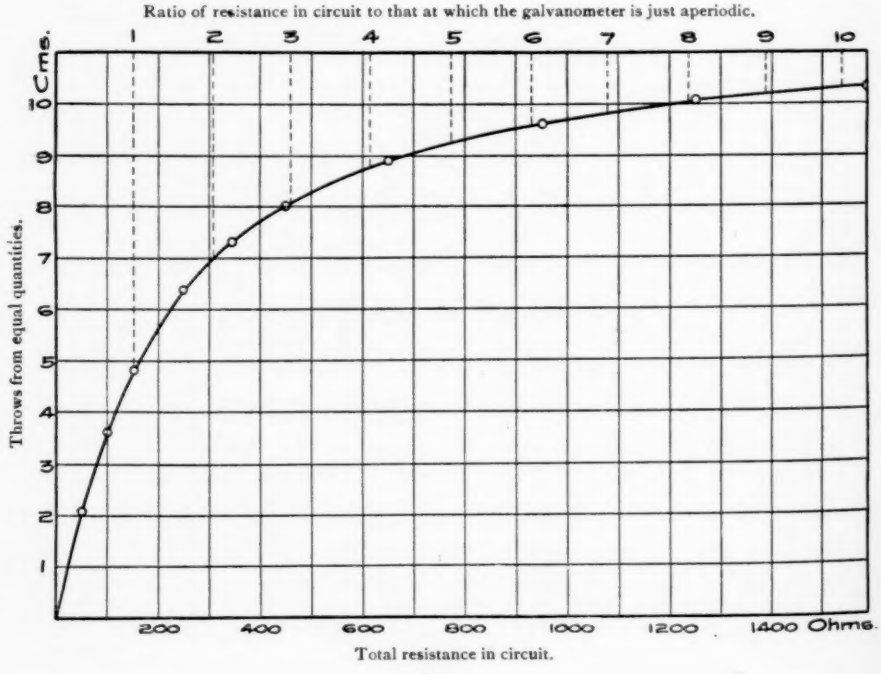

Fig. 1.

[1] H. Diesselhorst, Annalen der Physik, 1902, Vol. 9, p. 458.

mental curve showing the relation between the resistance in the circuit and the throws produced on a circular scale by equal quantities of electricity. The resistance of the galvanometer coil was 54 ohms, and its motion was just aperiodic when the total resistance in the circuit was 154 ohms. This curve applies to all galvanometers when the abscissas are plotted in terms of the ratios of the resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

If the field of the magnet is uniform (and radial) the damping with the same resistance is constant for throws of all magnitudes,[1] but as this condition is never fully realized (see § 6), the damping factor is only approximately the same. Since its value is much greater on closed than on open circuit work the proportionality of the throws is more affected[2] in the former than in the latter case. For this reason and on account of the greater sensitiveness it is preferable whenever practicable to employ the galvanometer on open circuit.

§ 3. Adjustment for Equal Deflections, Circular Scale, Increase of Period, Shunting of Galvanometer.

When the plane of the coil is parallel to the magnetic lines of force the deflections for the same continuous current should be equal in the two directions. This condition is the most desirable one for ballistic work also and can be obtained only by trial. Two short pointers[3] are attached, one to the coil and the other to a stationary part of the galvanometer. When the adjustment for equal deflections is completed the stationary pointer is bent until the tips of the two are in line. Future adjustments of the instrument can then be made with ease. These pointers are of special service for placing the coil on successive adjustments into the same part of the field to maintain the sensitiveness unchanged.

A circular scale of a radius equal to its distance from the axis of suspension of the coil is much to be preferred for accurate work

[1] O. M. Stewart, Phys. Rev., 1903, Vol. 16, p. 158.

[2] Donegan and Smith, Electrical Engineer, 1903, p. 830, have shown experimentally the presence on closed circuit of large variations in damping for throws of different magnitude.

[3] The Leeds and Northrup Company, at the suggestion of the writer, have already added these pointers to some of their galvanometers.

because the telescope is then in focus for all parts of the scale and the usual parallax is avoided. For ballistic throws the necessity of changing scale readings to angular measure or to equivalent[1] circular scale readings is also avoided.

A convenient way of changing the period of the galvanometer without changing the fiber or the coil is as follows: A brass wire with two lead balls attached to its extremities is bent in such a manner as to clamp easily onto the lower end of the coil. The moment of inertia of the system can be changed readily by bending the wire so as to alter the distance between the lead balls. Any desired period can be attained in this manner.[2]

In this type of galvanometers the constant is changed after an abnormally large deflection (see § 6). For this reason where large currents are liable to enter as in experiments requiring the balancing of the wheatstone bridge the shunting of the galvanometer must be made with special care while the balancing is in progress.

§ 4. Methods of Bringing the Coil to Rest.

As shown in § 1, the coil must return to the null position without crossing it more than a small amount. This is accomplished in the following manner:

(*a*) *In Open Circuit Work.* — If the galvanometer is aperiodic on closed circuit the coil is short-circuited after the throw at some point on its return, depending on the amount of damping present. If this is made at the proper place the coil reaches the null reading in the least possible time. Sometimes it is more convenient to close and open the circuit several times while the coil is in motion.

When the coil is finally at rest on the closed circuit, it is usually not at its true null point. A thermo-electric current existing in the circuit is deflecting the coil so that when the circuit is opened a vibration of several millimeters may occur. This is checked by quickly tapping the short-circuiting key while the coil is passing through the null point from the deflected position. In some cases

[1] Kohlrausch, Physical Measurements, 1894, p. 446.

[2] Since the writing of this paper a galvanometer made by Hartmann and Braun has been described in Biddle's Bulletin, Sept., 1906, which has attached to a pillar at the lower end of the coil a cross arm carrying at either end a small pan. Weights placed into these pans alter the moment of inertia of the system.

this is better accomplished by tapping several times while the coil is moving to the null point and checking the motion a little at a time, as in the case above.

If the galvanometer is not aperiodic on closed circuit the usual inductance coil is introduced and the motion checked by the movement of a magnet within this coil. To avoid the motion due to the thermo-electric currents the writer has for some years introduced a thermo-electric couple into the galvanometer circuit in addition to the inductance coil. By means of this the galvanometer is brought to the true null point before the circuit is opened. The thermo-electric couple suited for this purpose is one of brass wire, having the temper of a portion changed by heating to white heat. This portion forms a thermo-electric element with the remainder of the brass, so that by holding one's fingers on one side or the other it gives the proper thermo-electromotive force to overcome that in the circuit. Changing the pressure of the fingers upon the junction alters the thermo-electromotive force within the proper limits. Some, including the writer, prefer to use the inductance coil for this adjustment also, although it may require longer practice to attain ease in manipulation.

(*b*) *In Closed Circuit Work.* — On closed circuit work the best condition exists when the galvanometer is just aperiodic, requiring no attention to bring the coil properly to the null point. If the coil is over-damped a resistance can be temporarily introduced to lessen the damping. It must be removed, however, before the final reading is taken, as it alters the thermo-electric current in the circuit, causing a change in the null reading which in this case must be taken while the circuit is closed. If the coil is not damped sufficiently the inductance coil and magnet method must be employed as in part (*a*) above.

§ 5. Throws from a Vibrating Coil.

When a ballistic throw is to be taken while the coil is not entirely at rest the discharge must be made when the coil is at either turning point of its motion. The throw in either case must be computed from the natural null point and not from the point at which the throw originated as is sometimes stated. This is true for vibrations

small in relation to the throws and not for large ones. These vibrations need never exceed .02 or .03 cm. The writer, in his own work, never allows more than .01 cm. Table III. gives the throws obtained for the same quantity when discharged while the coil is at rest and again when at each of the extremes of its motion which was 0.3 cm., to either side of the null point and is greater than should be tolerated in practice. The larger variations in the throws of the last column are due to the inability of causing a throw

TABLE III.

Coil at Rest at 25.00 Cm.	Vibrating Coil at Elongation. 25.30 Cm.	Vibrating Coil at Elongation. 24.70 Cm.
35.53	35.53	35.52
35.52	35.53	35.52
35.52	35.52	35.54
35.53	35.52	35.51
35.525	35.525	35.523
25.00	25.00	25.00
10.525	10.525	10.523

at the exact time of the greatest elongation. The average values, however, agree with the deflection (column 1) made from the true null point. If the amount of vibration to each side of the null point exceeds 3 per cent. of the total throw an appreciable variation from the above condition is observed.

§ 6. THE VARIATION OF THE CONSTANT — THE DAMPING FACTOR.

It is well known that the strength of the magnetic field and the torsional moment of the suspending fiber change[1] with temperature and the moment due to the same impulse alters slightly on account of the expansion of the copper coil. Variations in the constant, however, are liable to occur during a single experiment even though the temperature remains constant. The observations given in Table IV. represent the magnitude of the throws produced by the same quantity of electricity at four different intervals during the same experiment. Between the sets of observations, however, the galvanometer coil had received deflections much larger than the throws

[1] B. O. Pierce, Am. Acad. Proc., 1893, **38**, p. 551.

employed. These deflections produced an apparently permanent change in the constant of the galvanometer. This is probably due mainly to a change in the direction of magnetization of the magnetic impurities in the coil as in the case of set and hysteresis considered in § 1.

TABLE IV.

Temperature °C.	Throws in Cm.	Change in Cm.	Change in Per Cent.
20.2	19.908 ± 3	——	——
20.3	19.893 ± 3	−.015	0.07
20.3	19.824 ± 3	−.084	0.42
20.2	19.445 ± 3	−.463	2.28

These changes render it impracticable for work of precision to assume that the constant of the galvanometer which is used for various deflections remains unchanged for any considerable length of time. Constancy can be assumed however for consecutive throws of the same magnitude providing that in the mean time no set has been given to the fiber and that the instrument has not been jarred or the temperature of the room changed.

The damping factor[1] $\sqrt{\theta_1/\theta_2}$ as mentioned in § 2 changes somewhat with the amount of throw, very little in a galvanometer of a nearly uniform (radial) field and a considerable amount in some galvanometers. In one galvanometer used by the writer the damping factor on open circuit for throws of

$$15.6 \text{ cm.} = 1.0243 \pm 1$$

and for

$$4.0 \text{ cm.} = 1.0193 \pm 3,$$

a variation of 0.5 per cent. In some galvanometers this variation was found to be as small as 0.2 per cent. but usually it is larger. This shows that if throws of unequal size are to be compared a correction must be made for the variation in the damping. This correction for large throws is somewhat uncertain because the

[1] The simplicity of this form makes it preferable to the logarithmic decrement still commonly employed. This simpler form is explained by Stratton and Milliken, Experiments in General Physics, 1896, p. 86; Zeleny and Erikson, Manual of Physical Measurements, 1902, p. 102; A. W. Smith, PHYS. REV., 1906, Vol. 22, p. 250.

amount of set in the fiber changes in the consecutive unequal vibrations to the opposite sides of the null point. It is therefore desirable whenever practicable to make the quantities compared nearly equal rendering this correction unnecessary and avoiding the usual requirement of an accurate adjustment of the scale with respect to the normal to the mirror.

§ 7. METHODS OF DETERMINING THE CONSTANT.

Since in this type of galvanometers, as was shown in § 6, the constant varies and must therefore be redetermined frequently, it is especially desirable that the method employed for its determination should be one which for the same degree of accuracy requires the least time. The four usual methods[1] are considered separately.

(*a*) The "Figure of Merit and Period of Vibration Method" can be employed in open circuit work only and usually is of little value where an accuracy greater than one half of one per cent. is required. The deflected coil is in a field of a different strength than when in its null position and therefore the figure of merit obtained from a continuous current has a value different from the one required for the ballistic constant. The length of time necessary for a determination of the constant and the uncertainty of the effect of the set in the fiber and of the hysteresis are additional reasons for discarding this method in work of precision.

(*b*) The Earth Inductor Method can be employed for determining the constant on closed circuit and by special construction on open circuit also. The determination of the strength of the magnetic field and of its variation in direction and intensity, especially in modern cities, render this method too difficult if not impracticable for the kind of work under consideration.

(*c*) The Standard Solenoid Method is the most practical of the three direct methods. The constant can be determined on either closed or open circuit and with an accuracy limited only by that with which the constants of the solenoid can be measured. The large size of the coil and the accuracy of construction required for work of the highest precision are its chief objections. (See § 8 and § 9(*a*).)

[1] Henderson, Practical Electricity and Magnetism, 1898, pp. 211–229.

(*d*) The standard condenser method, although an indirect one, is by far the most convenient of all the known methods. If the capacity[1] (free charge) and the temperature coefficient are accurately known it is capable of the highest attainable precision.

For open circuit work the condenser is charged by means of a standard cell and immediately discharged through the galvanometer, the circuit being opened before a measurable amount of the absorbed charge is liberated. This can be accomplished most conveniently by means of a special key, a Pohl commutator properly arranged as described in a previous paper above referred to, or by means of keys operated by a swinging pendulum. A single tap on an ordinary discharge key will also accomplish the same result with fair accuracy.

To obtain the constant for closed circuit work the condenser is discharged and its circuit opened as in the case above, but in addition, immediately after the discharge, the galvanometer circuit is closed, through the apparatus with which it is to be employed. In this way a known quantity of electricity is discharged through the galvanometer and the latter is damped during the whole[2] of its throw in the same manner as when otherwise employed in that particular circuit.

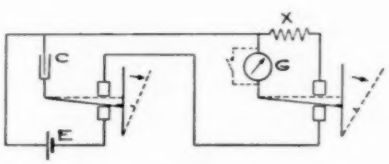

Fig. 2.

The connections are made preferably as shown in Fig. 2. The keys are operated in succession by a swinging pendulum[3] not shown

[1] A. Zeleny, Capacity of Mica Condensers, PHYS. REV., 1906, Vol. 22, p. 65.

[2] When the resistance in the circuit is small the damping is liable to be sufficient so that an appreciable effect on the amount of the throw is produced by the coil moving undamped during the short interval while the condenser is discharging and before the circuit is closed. Care must be taken to make this interval as small as possible. The time of discharge may be made as short as desired by decreasing the capacity of the condenser or the resistance of the galvanometer circuit, or both. The period of the galvanometer may also be increased to reduce the amount of the undamped movement. See also H. Diesselhorst, Annalen der Physik, 1902, Vol. 9, p. 712.

[3] Carhart and Patterson, Physical Measurements, 1900, p. 107.

in the figure. The key of Fig. 3 is the same as that already described,[1] with the addition of a contact piece, S, which closes the galvanometer circuit through the apparatus X immediately after the

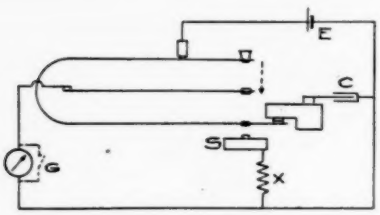

Fig. 3.

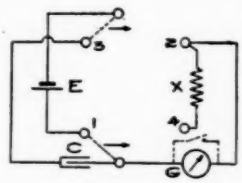

Fig. 4.

opening of the condenser circuit. The Pohl commutator, as shown in Fig. 4, may be employed for the same purpose. The height of the mercury in the cups is adjusted so that the contacts are made or broken in the order indicated by the numerals.

In any case the test for proper adjustment is made by varying either the speed of operating the key or the adjustment itself, so as to change the time before the closing of the galvanometer circuit and the time the condenser is allowed to discharge. This variation when made within proper limits should produce no appreciable effect on the throws obtained. If small variations produce an appreciable change the apparatus is not in proper adjustment.

When the circuit is closed an error may be introduced in the result by the thermo-electric current that usually exists in a closed circuit, which itself produces an appreciable deflection. The method of treatment of this is considered in § 9.

The only objection to this method is the uncertainty as to the condenser maintaining the same capacity value from year to year. The condenser plates are held together by the insulating material only, usually paraffin, in which they are imbedded. If the temperature of the room accidentally reaches an abnormally high value, the insulating material may soften sufficiently to allow the plates to change their relative position. For this reason the limiting temperature should be known and the condenser guarded against such extremes as may be known to affect permanent changes.

[1] A. Zeleny, PHYS. REV., loc. cit.

In the present state of our knowledge of condensers more or less doubt must exist as to their constancy for work of precision. When the condenser has not been exposed to abnormal influences, its capacity is known to remain constant for at least a considerable length of time. This makes it available as a working standard of the highest precision. Under present conditions, however, it must be tested from time to time. Since it is not practicable to send it often to the Bureau of Standards, a method of testing its constancy must be employed which is sufficiently simple to enable the determination to be made with ease and precision in any laboratory. The writer has employed for this purpose what he terms a "Standard Mutual Inductance Coil" (see § 8), which has proved to be very satisfactory.

8. The Standard Mutual Inductance Coil.

Two coils are wound one within the other on the same spool of specially well seasoned wood.[1] They are properly insulated and saturated in an insulating compound to prevent any displacement of the wire or any moisture entering the wood. When the coefficient of mutual inductance of these coils is once determined they can be employed in the same manner as a standard solenoid and make a much simpler and cheaper piece of apparatus, capable of at least as high a degree of accuracy.

The coefficient of mutual inductance is determined by comparison with the standard condenser to which it is intended to be a supplement employing the well-known relation[2]

$$Q_s = M\frac{I_p}{R_s}.$$

[1] Some other material may prove superior to wood. Rosa and Grover, Bulletin No. 3, Vol. 1, Bureau of Standards, have shown serpentine to possess magnetic impurities. Other similar substances must be proved free from them before being employed in standards.

Since the above footnote was written, J. G. Coffin, in the Bulletin of the Bureau of Standards, Vol. 2, p. 89, states that glass and plaster of paris are excellent materials for coils of small size and also gives the advantages of the use of marble. The writer, however, is aware that in at least some grades of marble there are veins of magnetic material.

[2] E. L. Nichols, Lab. Manual of Physics and Applied Electricity, 1894, Vol. 1, p. 243; Zeleny and Erikson, loc. cit., p. 111.

The current I_p in the primary coil is adjusted until the quantity Q_s in the secondary circuit is nearly the same as that given by the standard condenser. On account of the damping on closed circuit (see § 2 and § 9), the secondary circuit is opened by means of a proper key (Figs. 2, 3 or 4 modified), immediately after the passage[1] of the induced charge. When the resistance R_s in the secondary circuit is known the coefficient of mutual inductance M can be calculated and its true value obtained to within 1/100th per cent. This determination should be made before any possible change can occur in the value of the capacity as it had been standardized.

Future comparisons are made by assuming the coefficient of self-inductance to remain unchanged and the coil is used as a standard to determine the quantity discharged from the condenser, from which the value of the capacity is obtained in the usual manner,

$$CE = Q_1 = Kd_1$$

$$\frac{MI_p}{R_s} = Q_2 = Kd_2$$

and

$$C = \frac{d_1}{d_2}\frac{MI_p}{R_s E}.$$

When this value is the same as the original one the constancy of the capacity value is assured. Should any variation be detected it is reasonable to expect that the change occurs in the condenser. To avoid any uncertainty in such a case it is preferable to have two such standards of inductance wound in a different manner on separate spools of unequal diameters. The temperature coefficient of these standards, although very small, should be known or the observations must be taken always at nearly the same temperature.

This Standard Mutual Inductance coil may be used in the same manner as the standard solenoid for the measurement of quantities, in place of the condenser, but possesses the same disadvantage as the standard solenoid in requiring the determination of the value of

[1] The adjustment of the key is readily made on account of the very short time required for the discharge. It has been shown experimentally by E. Rutherford, Trans. New Zealand Institute, 1895, p. 182, that all the measurable part of the induced electricity passes in a few thousandths of a second.

a current and of a resistance for each observation, which renders it much less convenient for a working standard than the condenser. It is desirable therefore to use it only as a check on the constancy of the condenser.

§ 9. Correction for Thermo-Electric Currents.

Electrical circuits containing a galvanometer of the moving coil type are specially liable to thermo-electric currents. These can often be reduced in value and sometimes entirely avoided by screening the galvanometer from heat radiations and from air currents. Since these thermo-electric currents modify the amount of the ballistic throw they should be entirely eliminated. The writer has found the following method of removing them a most satisfactory one:

A secondary circuit P containing the storage cell E and a variable resistance box R, also includes a small part S of the galvanometer circuit. This part is composed of a few centimeters of the copper connecting wire. The resistance in R is adjusted until the electromotive force at the extremities of S is equal and opposite to the thermo-electromotive force in the circuit. This condition is tested by closing and opening the key K.

When it is not convenient to use this method the following corrections may be employed with a high degree of accuracy.

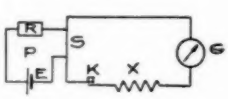

Fig. 5.

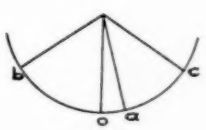

Fig. 6.

(*a*) *When Changing from Closed to Open Circuit.* — This is the most important case as in all closed circuit work it is desirable, as explained in § 2, to open the galvanometer circuit immediately after the discharge to avoid the damping. If the natural null point is at o (Fig. 6), when the circuit is closed, the apparent null point is at a due to the presence of a thermo-electric current. If no thermo-electric current is present a definite quantity of electricity produces a throw $ob = oc$. This same quantity when discharged while the coil is at the apparent null point a produces, when the circuit is opened

immediately, an apparent throw of *ab* on one side and *ac* on the other. The throws therefore must be calculated from the true null point, *o*, as it is on open circuit, and not from the apparent one, *a*, observed on closed circuit.

The case is practically the same as that of the throw obtained from the maximum elongation of a vibrating coil as described in § 5.

(*b*) *Changing from Open to Closed Circuit.* — In experiments with the earth inductor and with ballistic galvanometer methods for determining the magnetic properties of iron, it is inconvenient to open the galvanometer circuit before the coil moves an appreciable amount. In such cases it is preferable to determine the constant on closed circuit. If the condenser is employed for this purpose

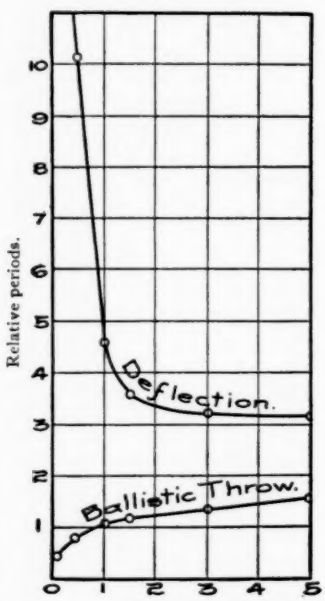

Fig. 7. Ratio of resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

the galvanometer must be closed through the inductance apparatus immediately after the discharge so as to be affected by the proper amount of damping (see § 7, *d*). The throw obtained is influenced by the presence of the continuous thermo-electric current and the result is not the algebraic sum of the maximum effects due to each

quantity acting alone because the period of the coil is different for continuous currents and for the ballistic throws. The relation of the periods is roughly shown in Fig. 7 for different values of the resistance in the circuit. The value of the correction to be made for the presence of the thermo-electric current depends upon the amount of damping and can be obtained by aid of the curves of Fig. 9 or from the curve of Fig. 10.

The method by which these curves were obtained is as follows:

The data were taken from a Leeds and Northrup open-coil galvanometer of 135 ohms resistance. The suspension was 1.5 mil phosphor bronze strip and the circular scale has a radius of 51.4 cm. The set on reversal from 15 cm. was 0.22 cm. The uniformity of the field on the side that the throws were taken was such as to cause the deflections on a circular scale to be proportional to the current to within 0.1 per cent. The resistance at which the galvanometer is just aperiodic was first determined by the method described by Wenner[1] as shown in the curve of Fig. 8. The curve

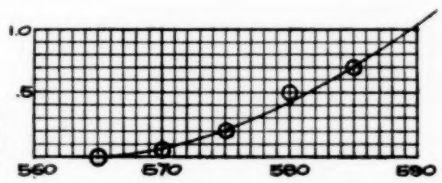

Fig. 8.

indicated by the points was extended so as to meet the axis of abscissas. This gives 565 ohms as the resistance at which the galvanometer is just aperiodic and the value is probably correct to within 3 or 4 ohms or about 0.7 per cent.

The apparatus was then arranged as shown in Fig. 2 with the addition of the secondary circuit described above in this section and shown in Fig. 5. This secondary circuit was employed to cause any desired current in the galvanometer, and for experimental purposes took the place of a thermo-electric current. The keys were adjusted so that the galvanometer circuit was closed in 1/100th second after the beginning of the condenser discharge. The period of the

[1] PHYS. REV., 1906, Vol. 22, p. 192.

throw on open circuit was 4.8 seconds and on closed circuit, containing the galvanometer only, it was 4.4 seconds.

It was shown that for small currents giving a deflection of less than 5 millimeters the value of the correction in per cent. of the total deflection given by the current was numerically the same, near enough for the required purpose, whether the throw was large or small [1] and whatever the direction of the thermo-electric current with respect to the throw. The correction, however, is to be added to or subtracted from the observed throw depending upon whether the electric current is in the opposite or in the same direction as the throw.

It was also shown that for currents giving a deflection of 2 centimeters the correction to be added differed considerably from the one to be subtracted but the average of the two gave the same percentage value as that obtained from the smaller currents. For the purpose of obtaining greater observational accuracy it was considered desirable to use the average correction obtained from the larger currents. The value of the corrections is given in Table V, and plotted in the Curve *B* of Fig. 9. To make the correction applicable to all galvanometers damped in a similar manner the resistance in the circuit is given in terms of the resistance at which the galvanometer is just aperiodic. The total resistance in the circuit is represented by R_c and the resistance at which the galvanometer is just aperiodic by R_{ap}.

TABLE V.

Resistance Ratio. R_c/R_{ap}.	Correction in Per Cent. of Thermo-electric Deflection.	Resistance Ratio. R_c/R_{ap}.	Correction in Per Cent. of Thermo-electric Deflection.
0.25	5.5	3	57.8
0.379	11.0	4	65.1
0.5	15.0	5	69.6
1	27.8	7	75.8
1.5	39.6	10	80.6
2	48.1		

In order to simplify as far as possible the method of obtaining the ratio R_c/R_{ap}, the following method was employed for obtaining

[1] The magnitude of the throws must be at least three times the deflection produced by the thermo-electric current.

the data for the Curve *A* of Fig. 9, from which the ratio, providing it is greater than unity, can be obtained by means of one observation.

It was first observed that the distance the coil moves beyond the null point after a deflection is proportional to the deflection. It was found that a motion of 3 cm. beyond the null reading pro-

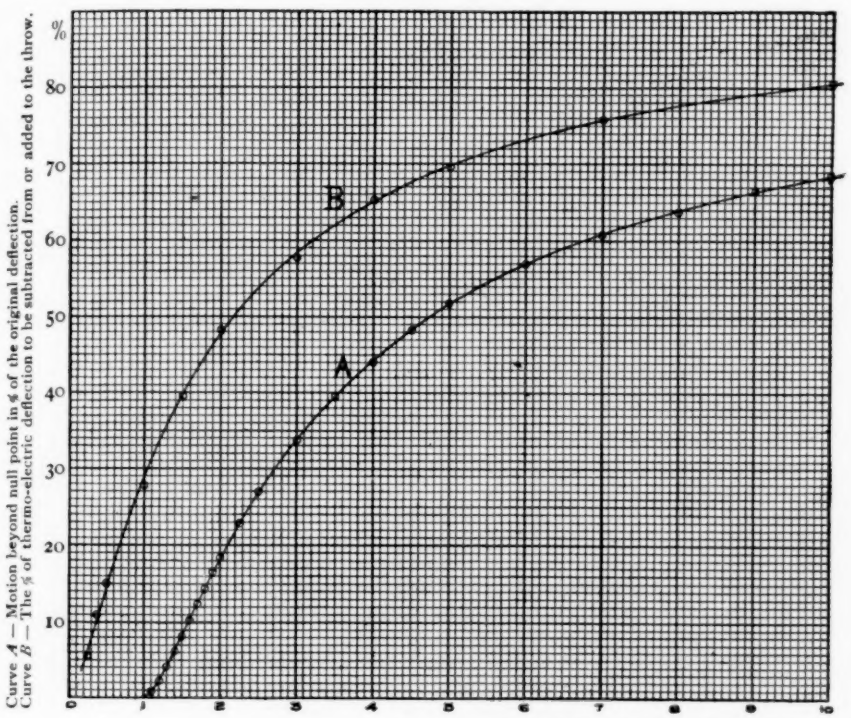

Fig. 9. Ratio of the resistance in the circuit to the resistance at which the galvanometer is just aperiodic.

duced no appreciable set by the reversal, in the particular galvanometer employed. The deflections used were 20, 10 and 5 cm., depending on the damping in the circuit, the object being to keep the motion beyond the null point as large as possible without exceeding 3 cm. The apparatus was the same as in the case above, but the deflecting currents from the secondary circuits were made larger. This secondary circuit was opened and the distance the coil moved beyond the null point was observed with various resist-

ances in the galvanometer circuit. The data of Table VI. give the percentage of the original deflection the coil moved beyond the null point for various resistances in the circuit. These also are expressed in terms of the resistance at which the galvanometer is just aperiodic so as to be applicable to any galvanometer.

TABLE VI.

R_c/R_{ap}	Motion Beyond Null Point in Per Cent. of Original Deflection.	R_c/R_{ap}	Motion Beyond Null Point in Per Cent. of Original Deflection.	R_c/R_{ap}	Motion Beyond Null Point in Per Cent. of Original Deflection.
1.01	0.02	1.7	12.49	4	44.02
1.05	0.35	1.8	14.45	4.5	48.10
1.1	0.92	1.9	16.50	5	51.85
1.2	2.26	2	18.43	6	57.00
1.3	4.05	2.25	22.93	7	60.90
1.4	6.10	2.5	27.00	8	63.93
1.5	8.15	3	33.75	9	66.46
1.6	10.32	3.5	39.63	10	68.40

If it is desired to find what per cent. of the thermo-electric deflection must be applied as a correction to any ballistic throw, the coil is allowed to return after the throw in its natural way and the distance it moves beyond the null point[1] is observed. The value of this distance in per cent of the observed throw is calculated. From this the value of R_c/R_{ap} is obtained by use of Curve A, Fig. 9, and from this value in turn the desired percentage correction by the use of Curve B. Since the thermo-electric deflection rarely exceeds 2 mm. an error in the correction of less than 2 per cent. is not appreciable, and it is believed these curves apply to any galvanometer within that limit. The curve of Fig. 10 is derived from the curves of Fig. 9 and gives the values of the percentage correction more directly. Several galvanometers were tested having different resistances and different types of coils, and in each case the correction obtained from the curves agreed with the experimental results.

To illustrate the manner in which the correction is made, suppose a thermo-electric current which gives a permanent deflection of 0.20

[1] In practice the thermo-electric current alters the null reading on changing from open to closed circuit. This altered null reading must be employed in the calculation of the distance the coil "moves beyond the null point," while the throw itself is calculated from the original null point on open circuit.

cm. when acting alone, and assume the ballistic throw when affected by this thermo-electric current to be 10.00 cm. in the same direction, and that the coil on its return moves 2.7 cm. beyond the apparent null point, *i. e.*, 27.0 per cent. of the observed throw. From Curve *A*, $R_c/R_{ap} = 2.51$, and from this again Curve *B*, gives the

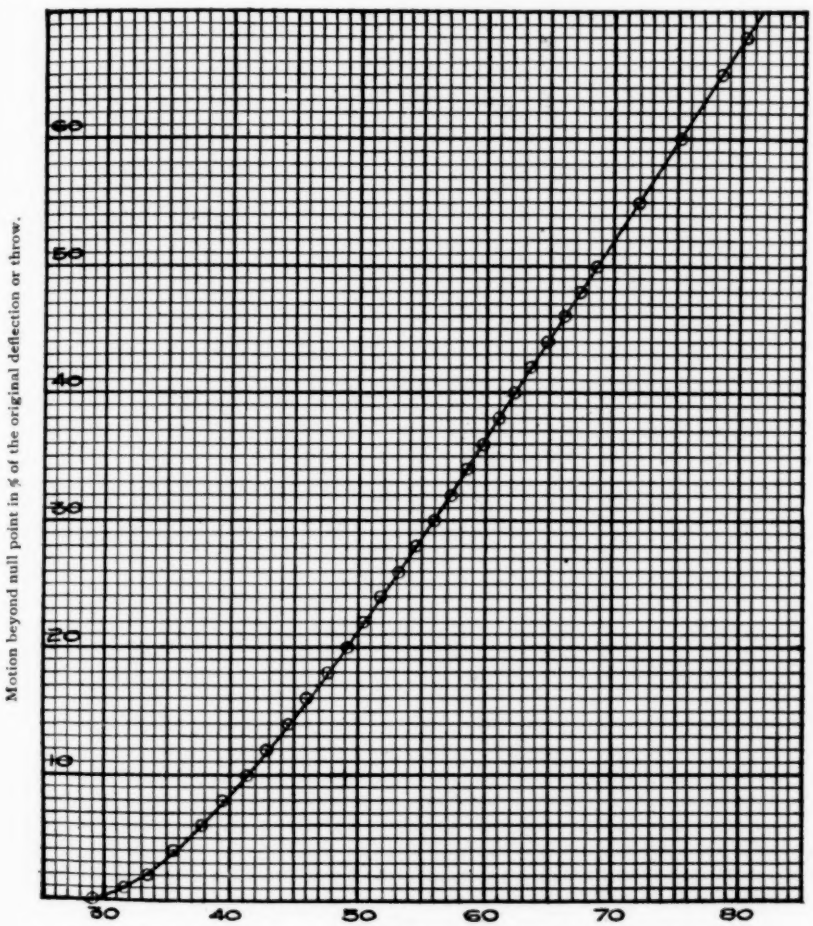

Fig. 10.

value of the correction to be applied as 53.9 per cent. of the deflection produced by the thermo-electric current. The correction, therefore, is 0.11 cm. and in this case is to be subtracted, making

the corrected throw = 9.89 cm. From the curve of Fig. 10 the 27.0 per cent. gives the correction of 53.9 per cent. more directly, and this is the curve to be employed in practice.

§ 10. GALVANOMETER RESISTANCE BY A METHOD OF DAMPING.

The Curve *A*, Fig. 9, may also be employed for an approximate determination of the galvanometer resistance.[1] The distance the coil moves beyond the null point is observed on closed circuit, and again with an additional known resistance. If on closed circuit the coil moves *n* per cent. of the original deflection beyond the null point, from Curve *A*, $R_c/R_{ap} = a$. If an additional resistance of *R* ohms causes the distance the coil moves beyond the null point to increase to *m* per cent.,

$$\frac{R_c + R}{R_{ap}} = b.$$

Then

$$\frac{R_c}{R_c + R} = \frac{a}{b},$$

and R_c, the resistance of the original galvanometer circuit $= aR/(b - a)$. This is often a very convenient method and gives the resistance with sufficient accuracy for many purposes.

§ 11. CONCLUSION.

The constant of a moving-coil galvanometer is a variable quantity depending on several conditions. For work of the highest precision the unknown quantity must be compared with a known one of nearly equal magnitude and the two throws must be obtained in immediate succession. A set in the fiber must be avoided by always taking the throws in the same direction and stopping the motion of the coil on its return before it crosses the null point. The first throw taken after a period of rest and any throw after which a change in the null reading is observed must be discarded. In the latter case the readings following must not be compared with those taken before. Whenever it is practi-

[1] The results obtained for various types of galvanometers by using this method, agree to within 1 per cent. of the true values. On account of the variations in the intensity of the magnetic field being different in different galvanometers it was not considered practical to attempt measurements with a greater accuracy.

cable the galvanometer should be used on open circuit. It is then more sensitive and the quantities more nearly proportional to the throws.

The mica condenser (free charge capacity) is by far the most convenient working standard for the comparison of electrical quantities. Its capacity should be tested from time to time on account of possible permanent changes. This is most conveniently accomplished by means of a standard mutual inductance coil whose coefficient is determined by comparison with the condenser when its capacity is first measured.

On closed circuit work, whenever it is practicable, the galvanometer circuit should be opened immediately after all the measureable part of the electrical discharge has passed through it. The quantities are then compared with the galvanometer on open circuit. When it is necessary to leave the galvanometer circuit closed during a throw the induced quantity can be compared with the known one from the condenser by discharging the condenser through the galvanometer and then immediately closing the circuit.

When during a comparison of the quantities the circuit is changed from a closed to an open one or the reverse, the thermo-electric currents of the circuit must first be eliminated or a correction made for their effect.

Observing the precautions and using the methods described in this paper, the moving-coil galvanometer can be employed with ease for measuring electrical quantities to the highest degree of accuracy attainable with direct deflection methods.

PHYSICAL LABORATORY,
THE UNIVERSITY OF MINNESOTA,
June 12, 1906.

OPTICAL PROPERTIES OF CARBON FILMS.[1]

BY HERBERT A. CLARK.

PURE carbon has been generally supposed to be a black body. Rosicky[2] in 1878, and later Stark,[3] investigated smoke films. The latter considered a smoke film as a turbid medium of air and carbon, and concluded that its dispersion is between that of air and of pure carbon. Ångström,[4] working in the infra red, obtained a rapidly increasing absorption in the case of lampblack from a wave length of 9,000 $\mu\mu$ down to 690 $\mu\mu$. Wood,[5] in 1901, using prismatic methods on smoke films, found the red rays retarded more than the blue, from 663 $\mu\mu$ to 414 $\mu\mu$; and, using interference methods, that films deposited on plate glass inside an electric lamp globe seem to show the same. For the latter films, he obtained a refractive index of 2.2 for the *D* line.

About the same time, E. L. Nichols[6] and Blaker[7] found that carbon rods and incandescent lamp filaments, both "treated" and "untreated," show, as their temperature increases, a more rapid increase in the radiation of the spectrum in the yellow than in the red or blue. Dr. Brace suggested[8] that the electro-magnetic theory shows that this increase in the radiation and the anomaly as found by Wood, both point to an absorption band in the yellow. Nichols[8] had found a maximum of absorption in the visible spectrum at the wave length 520 $\mu\mu$, in the case of lampblack. B. E. Moore and Ling[9] found the same in deposits on incandescent lamp globes at

[1] Read in part before the Am. Phys. Soc. at Chicago, April, 1905; and in part before the meeting at New York, December, 1905.

[2] Rosicky, Wiener Berichte, 78, II., p. 407, 1878.

[3] Stark, Wied. Ann., Vol. 62, p. 353, 1897.

[4] Ångström, Wied. Ann., Vol. 36, p. 715, 1889.

[5] Wood, Phil. Mag., VI., Vol. 1, p. 407, 1901.

[6] Nichols, PHYS. REV., Vol. 13, p. 129, 1901.

[7] Blaker, PHYS. REV., Vol. 13, p. 345, 1901.

[8] Nichols and Blaker, PHYS. REV., Vol. 13, p. 378, 1901.

[9] Nichols, Am. Jour. Sc., Vol. 34, p. 277.

the wave length 635 $\mu\mu$, from "treated" filaments, but not from "untreated" filaments. Neither Rosicky[1] nor Stark[2] noticed this maximum in the absorption.

Nichols,[3] working also with a prism of asphalt, which he considers a solution of carbon, determined the refractive index at four points in the red and yellow; and found an anomaly at a wave-length of 568.2 $\mu\mu$, with a refractive index of 1.6339. In the infra red, he found the absorption of asphalt to be very similar to Ångström's[4] values for lampblack, only that the change is much more abrupt.

None of these investigators, however, so far as I know, have determined by direct methods, the reflection, the refraction, and the absorption, all from the same specimen of pure carbon in a dense form. At Dr. Brace's suggestion, I have attempted to do this. This problem presupposes the use of transparent films of carbon. As yet, films of two kinds only have been considered; namely, those produced by Wright's[5] cathode method of deposit, and those obtained from the inside of incandescent lamp globes.

Making the Films.

Longden[6] has shown that the character and the rate of deposit from a cathode upon a glass plate in a vacuum, depend upon the vacuum, the electromotive force, the current density over the cathode surface, and the distance from the cathode to the glass plate, as well as upon the material of the cathode. A vacuum tube (shown in cross section in Fig. 1) was so constructed that these conditions might be varied at will to produce the best results. It was made of two ordinary low form glass bell jars; the flanges of which were ground on a plane surface, so that they fit closely together, flange to flange. C is a carbon cathode, surrounded by mica. A hole in the upper mica sheet at D allows the cathode discharge to deposit carbon on the lower face of the glass plate, A. This plate is supported by the anode, B, a sheet of brass. The anode, in turn,

[1] Rosicky, l. c.
[2] Stark, l. c.
[3] Nichols, Phys. Rev., Vol. 14, p. 204, 1902.
[4] Ångström, l. c.
[5] Wright, Am. Jour. Sc., III., Vol. 13, p. 49, 1877.
[6] Longden, Phys. Rev., Vol. 11, p. 40, 1900.

is carried by a metallic stem, *M*, the lower end of which is of square cross section; the upper end is threaded. By turning the ground joint, *H*, the glass plate may be moved into the cathode stream, or out of it; by turning *K*, the distance between cathode and plate can be varied. The electric circuit in the tube is from the anode terminal, *F*, through a wire to a threaded nut in *K*; through the stem, *M*, to the anode, *B*; through the gas to the cathode, *C*; through a wire protected by a glass tube to a mercury cup, *E*; thence to the cathode terminal, *G*. Ordinary stop cock grease served to make the joints, all of which are ground glass, perfectly air tight. The cathode was made by combustion of granulated sugar, which is considered by chemists to yield the purest form of carbon, excepting the diamond.

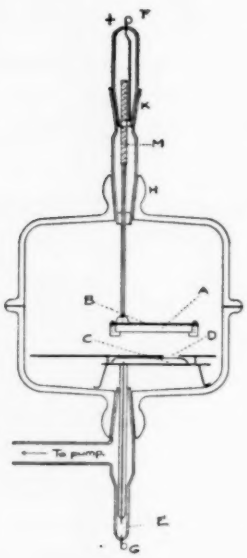

Fig. 1.

The films were deposited in atmospheric air which had been dried carefully, at low pressure, in contact with phosphorus pentoxide. A high potential storage battery served as a source of current, which was unidirectional. The best conditions for depositing carbon in air were found by trial to be as follows: a voltage of about 1,100; a current density of about .05 milliampere per square millimeter of cathode surface; a distance from cathode to glass plate of about fifteen millimeters; and such a gas pressure that the Crookes' dark space extended 5 or 6 millimeters from the cathode. The gas pressure was not measured definitely, but was less than one millimeter of mercury. Since slight changes in gas pressure change the resistance of the tube very appreciably, a galvanometer in series with the tube was used to determine the constancy of the gas pressure.

The films, under carefully adjusted conditions of deposit, were slightly prismatic, were reddish brown or black in color by transmitted light, appeared perfectly homogeneous and highly polished to the naked eye, varied in thickness from 0 to .10 μ and in transparency from 0 to 100 per cent., according to the thickness.

Viewed by reflected white light, they show beautiful interference bands, up to five or ten orders. They are almost as easily injured by rough usage as is a half-silvered coat on an interferometer plate, but seem to be independent of time changes except for a cracking and scaling off of the thicker portions. Those used were about one year old when measurements were made.

The second kind of films was unusually heavy deposits found on the inside walls of an ordinary incandescent lamp, which had been run at an abnormal voltage. The exact composition of the carbon filament in this case is not known.

Test for Anomalous Dispersion.

The supposed pressure of an anomaly in the refractive index curve of carbon led to making a test for this, by a method devised by Dr. Brace.[1] If light reflected from the two surfaces of a thin film is resolved by a prism or a grating, the spectrum will be crossed by dark lines, or "spectral bands," at those wave-lengths for which destructive interference occurs. If this film has an anomaly in its dispersion, the "spectral bands" will be variable in width; but they will coincide in width with similar bands from an air film at a maximum or a minimum point in the dispersion curve, if the order of interference is the same for the two films at this wave-length. Between the maximum and the minimum points, the "air bands" will be narrower than those of the medium; elsewhere the "air bands" will be the broader. Or, if the anomaly is very slight, the maximum and minimum may coincide, giving a point of inflection; in this case, the "air bands" will be broader on both sides of this point.

Two sets of "spectral bands" can be compared directly for this test, either with the eye or by photography, by means of a device shown in Fig. 2. A second collimator, H, is inserted into the side of the usual collimator, C, of an ordinary spectrometer. A mirror, A, set at an angle of 45° to either line of collimation, covers half the cross-section of C. The upper half of one collimator slit and the lower half of the other are covered with black paper. Then two spectra are seen in the eye-piece of the observing telescope;

[1] Brace, PHYS. REV., Vol. 21, p. 291, 1905.

one in the upper half of the field, the other in the lower. By carefully adjusting *A*, these two spectra may be made to coincide throughout, line for line, the dividing line between the two becoming almost a vanishing line. *B* is a glass plate holding a thin film of the substance under investigation. A very small mirror, *D*, shown in the enlarged diagram, Fig. 3, enables light to be reflected at nearly normal incidence, from the film into the collimator. The use of this small mirror is far more satisfactory than that of a small, totally reflecting prism inside the collimator, one 45° edge of the

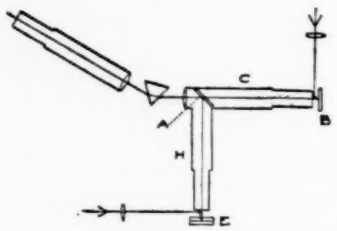

Fig. 2.

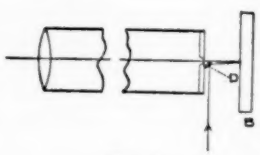

Fig. 3.

prism serving as one edge of the slit; as the prism produces too much diffuse radiation inside the collimator, when highly absorbing substances are examined. Reflection from the two surfaces of the film gives "spectral bands," which may be compared with similar bands obtained from the surfaces of the air space between two glass plates, *E*. If this space is prismatic, "air bands" of any desired order, to coincide with the order of those from the film, may be brought into the telescope by sliding along the plates, *E*, in front of the slit. A Nernst lamp was used effectively as a source of light. Ten "spectral bands" between wave-lengths of 687 $\mu\mu$ and 472 $\mu\mu$ were obtained; but no anomaly was detected, although the irregularity in the dispersion curve (*A*, Fig. 9) suggests a very slight anomaly in the region of the *C* line.

THE INTERFEROMETER SYSTEM.

In determining the refractive index, interference methods were used entirely, in preference to prismatic. The interferometer employed was of the Jamin type, essentially the same as the one used by Cartmel.[1] Certain slight changes in arrangement and

[1] Cartmel, Phil. Mag., VI., Vol. 6, p. 214, 1903.

adjustment proved so advantageous, however, that a description is here given. In Fig. 4, *a* is the source of light, a Nernst glower; *b* is an adjustable slit in a screen; *c* is a nicol prism; *d* and *d'* are achromatic lenses of 25 cm. focal length; *e* and *e'* are the half silvered plates, and *f* and *f'*, the full silvered mirrors of the interferometer; *k* and *k'* are mica strips, the latter being a compensator;

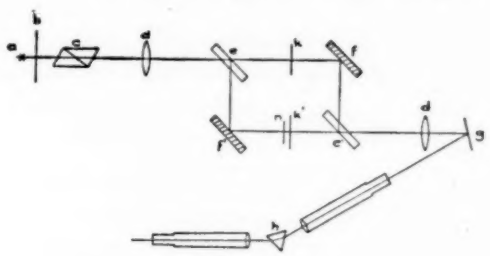

Fig. 4.

n is the film under investigation; *h* is a spectroscope; and *g* is a mirror, which allows the spectroscope to be placed in such a position that the operator can easily reach all parts of the system without changing his position.

The interferometer plates are first adjusted for parallelism by alignment on an object at a distance of at least two miles, instead of only two or three hundred meters. It was found by trial that the consequent higher degree of accuracy in the parallelism of the plates made the "spectral bands" much more distinct and clear. The two light paths, *efe'* and *ef'e'*, are next made exactly equal by examining a very near object through them with the naked eye, and then the colored fringes of white light come into view. These fringes are then made vertical. No "spectral bands" will appear in the spectroscope as yet, for they are due to a slight difference in the two light paths. This difference is obtained by moving one of the mirrors *f* or *f'*, parallel to the direction of the ray from *e* to *f*. No further adjustment of the interferometer is needed to give clear, sharp "spectral bands," white light being used.

The nicol prism is turned so that its plane of polarization is vertical; consequently, nearly all of the light that is reflected from the half-silvered plates, comes from the rear (the half-silvered) surface. This makes the "spectral bands" more distinct, by eliminating all

but one set of interfering rays. In case the lens, *d*, forms an image of the slit, *b*, upon the film, *n*; and the lens, *d'*, casts an image of that in turn upon the slit of the spectroscope, no "spectral bands" are seen. But let the spectroscope now be moved a few centimeters toward *g*, then bands are seen very plainly. In practice, however, the lens, *d*, is placed to form an image of the slit, *b*, upon the interferometer plate *e'*; then the lens, *d'*, produces an image of the film, *n*, upon the slit of the spectroscope. This allows a concentration of light upon the highly absorbing film under investigation at *n*, without recombination of the interfering rays into white light by the lens, *d'*.

Positions in the spectrum were determined by means of a tangent screw attached to the telescope, the micrometer head being about 6 cm. in diameter. This enabled the readings to be taken much more easily and quickly than if the usual circular scale had been used; and also made the order of accuracy of the readings somewhat higher, about the same as that of the settings. This method is much preferable to the use of a micrometer eyepiece, because of the unavoidable parallax while examining "spectral bands." The compensator *k'*, is the same kind as was used by Cartmel.[1] In addition, however, another piece of mica, *k*, of exactly the same thickness and with its optic axis in the same direction, is put in the other interferometer path. Another plate of glass of exactly the same thickness and composition as that of the one upon which the film, *n*, is deposited, is placed next to *k*. The two light paths, *efe'* and *ef'e'*, are thus identical except for the presence of the film itself and for the slight increase of length of one light path *in air* over that of the other. Any observed differential dispersion, then, is not affected by the presence of the compensator or of the glass.

THE REFLECTION ATTACHMENT.

To measure the absolute reflection of any surface directly, it is essential that the path of the beam of light which is reflected and the path of another beam, which is used for comparison, shall be identical from the source to the eye, except that the first beam suffers reflection from the surface considered. It is also essential that

[1] Cartmel, l. c., p. 217.

the two beams shall be identical in intensity at the source; or else, that each can be compared directly with a third, the intensity of which varies exactly with that of the beam being examined. The first essential condition is realized by the use of a reflection attachment for the spectrophotometer, described below. In the second condition, two alternatives are offered. The first is difficult to attain. The second is readily realized by the use of the Brace spectrophotometer,[1] to one collimator of which the above attachment is fastened. The illumination of the two collimator slits comes from opposite sides of one point in an acetylene flame. Any gradual variations in the intensity of the source, then, can not affect the results, unless the intensity of the two sides of the flame at the same point should vary unequally; which is not likely. The adjustments of the spectrophotometer have been given by Tuckerman.[2]

The instrument readings taken, when the illumination for one collimator slit is reflected from the surface under consideration, are designated as the "reflection readings"; those taken when an identical beam does not suffer this reflection, the "direct readings." The absolute value of the reflection follows directly, then, as the ratio of the "reflection reading" to the "direct reading." The upper part of Fig. 5 shows a plan and the lower part, a side elevation, of the reflection attachment. A is the slit end of one collimator; B and C are small, totally reflecting prisms. B may be rotated by means of a crank, D, about an axis approximately parallel to the line of collimation, HK, through an angle of nearly 90°, fixed by adjustable stops (not shown in the figure). Prism C is arranged to slide from the position shown in the figure to a position directly over prism B, by means of the long guard arm E. Projections at either end of E are carefully fitted into slots in the bed plate, F. This allows the motion of C to be made parallel to the line of collimation. This motion is also regulated by adjustable stops (not shown). The operation is as follows. Light from the source behind strikes prism B, is reflected down to the horizon-

[1] Brace, Phil. Mag., V., Vol. 48, p. 420, 1899; also Astrophys. Jour., Vol. 11, p. 6, 1900.

[2] Tuckerman, Astrophys. Jour., Vol. 16, p. 145, 1902.

tal plate, *M*, whose reflection is to be measured, then up to prism *C*, then into the slit of the collimator, *A*; and a "reflection reading" is taken. Prism *B* is next rotated (nearly 90°) until it reflects the light up; prism *C* is moved over it, reflecting the ray again into the slit; and a "direct reading" is taken. To make the light paths in the two collimators symmetrical, two prisms corresponding to *B* and *C*, cemented together with Canada balsam, were placed in front of the other collimator slit.

The adjustment of the reflection attachment is as follows. An acetylene flame is put at the ocular slit of the spectrophotometer,

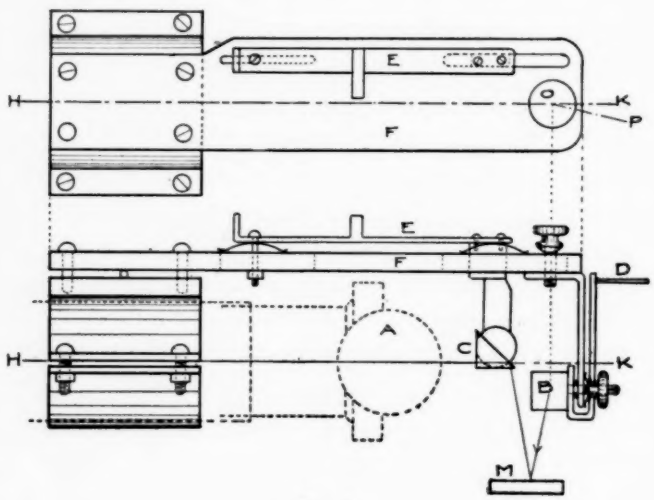

Fig. 5.

whence light passes through in a direction opposite to the usual one; hence the beams from the two collimators reach the plane in which is placed the source, ordinarily. Between each collimator slit and this plane is an achromatic condensing lens, forming an image of each slit upon the plane. By suitable adjustments, these images of the two slits are made to coincide, for both the "reflection" and the "direct reading" positions of the movable prisms. Further adjustments will make both the "reflection" and the "direct reading" beams pass through the same part of the condensing lens, as is determined by cross wires over the lens. If, now, prism *B* be tilted on its base through a definite angle, and its axis of rotation be

moved about a vertical axis through a definite angle to a position, *OP*, light will pass through it perpendicular to both faces, and along identical paths, in its two positions; except that for one, the beam enters *B* where in the other it emerges, and *vice versa*.[1] Further, the objective of the telescope, which has a focal length of 300 mm., is diaphragmed down to 5 mm. in diameter, making an angular aperture of about 1°. The light paths for the two positions of prisms *B* and *C* are now identical from source to ocular slit, except for that part between them, where reflection takes place in one case. That this distance is greater for the "reflection readings" than for the "direct readings" is immaterial, if the intensity of the source over the area considered is uniform at any one instant. This area is about 1 sq. mm. for an angle of incidence of 5.75° upon the plate *M*, whose reflection is to be measured. At this angle, determined by a distance of 2 cm. between *B* and *M*, all of the readings were taken. The advantages of this method are: (1) the absolute reflection is measured directly for the chosen angle of incidence, as is shown above; (2) since the reflecting surface is horizontal, the method may be used for liquids; and (3) the area considered is small, — not greater than 0.4 mm. square in this case, — thus giving the value at a point, instead of an average value over a surface. The surface as a whole, therefore, need have no definite curvature, — it is necessary only that it be plane over a very small area.

Transmission.

Measurements of the transmission of the films were made in the visible spectrum with the Brace spectrophotometer. Tables II. and III. give two sets of readings for the transmission of film No. 9, a cathodic film, at a point where its actual thickness is 4.67 μ; Table I., of film No. 15, an incandescent lamp film, the thickness being .236 μ. The "transmission" is given as the ratio of the intensity of light through the film, to that of light through the clear glass upon which the film is deposited, the two intensities being determined at places not more than 4 mm. apart. These results are shown graphically in Fig. 6; curve *A* is an average from the two sets of readings on film No. 9; curve *B*, for film No. 15. If there is a

[1] It is thus necessary to select a prism whose faces are polished alike.

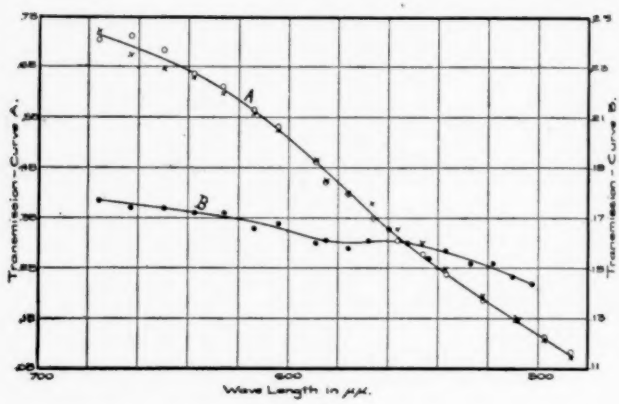

Fig. 6.

TABLE I.

Transmission of incandescent lamp film, No. 15; *thickness,* 0.236 μ.

Wave-length.	Transmission.	Wave-length.	Transmission.
—	—	576	.158
676	.177	568	.161
663	.174	560	.166
650	.174	552	.160
638	.172	544	.154
626	.172	537	.157
614	.166	527	.152
604	.168	518	.152
589	.160	510	.147
585	.161	502	.144

TABLE II.

Transmission of cathodic film, No. 9; *thickness,* 4.67 μ.

Wave-length.	Transmission.	Wave-length.	Transmission.
676	.720	566	.380
663	.675	556	.330
650	.646	546	.304
638	.630	537	.250
626	.596	522	.199
614	.560	508	.148
604	.526	497	.106
589	.465	486	.074
585	.425	477	.054
576	.401		

TABLE III.

Transmission of cathodic film, No. 9 ; *thickness,* 4.67 μ.

Wave-length.	Transmission.	Wave-length.	Transmission.
676	.702	566	.350
663	.711	556	.305
650	.681	546	.277
638	.635	537	.237
626	.611	522	.187
614	.563	508	.147
604	.531	497	.114
589	.461	486	.083
585	.422	477	.055
576	.397		

maximum in the absorption, such as was found by Nichols[1] for lampblack or by Moore and Ling[2] in the case of incandescent lamp deposits, it is very slight.

The transmission in the ultra-violet was obtained in a qualitative way by means of a Schumann quartz spectrograph. An induction coil arc between terminals of an alloy of cadmium, zinc and aluminium was the source of light. The well-known method of "crossed prisms" was used. Very thin cathodic films on quartz plates were placed before the slit, with the refracting edge of the slightly prismatic film perpendicular to the slit. Under these conditions, photographs were taken with varying times of exposure. If the film over one end of the slit is thin enough to transmit light of a certain wave-length, but thick enough at the other end to be opaque for the same wave-length, the effect upon the photographic plate will be an apparent shortening of the slit. Fig. 7, showing three exposures on one plate, brings out this effect plainly. The faint exposure was a short one, taken before the film was put in place, to locate points in the spectrum. The other two exposures, as well as every other one taken with the film before the slit, show an exposure over the

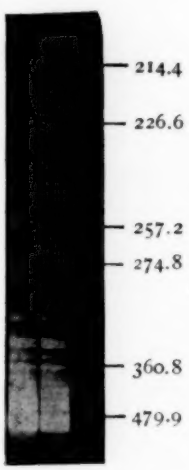

Fig. 7.

[1] Nichols and Blaker, l. c.

[2] Nichols, Am. Jour. Sc., Vol. 34, p. 277.

whole length of the slit at the red end at a uniform decrease in length for shorter wave-lengths as far as 226.6 $\mu\mu$; beyond this, the absorption is apparently complete as far out as 189.6 $\mu\mu$, the last wave-length detected when the slit is not covered by a film. A true absorption band, if present, would have shown first a decrease in length, then an increase.

REFLECTION.

The reflection was measured as previously described. No attempt was made to polish any film, — a camel's hair brush will scratch the hardest cathodic carbon surface. In every case, the best reflecting portion of the surface was selected for measurements, which were made on the air surface. These were probably affected very slightly by reflection from the clear glass surface on the back side of the glass plate upon which the film was deposited. A pronounced and puzzling waviness in the reflection curves as first obtained, which varied from point to point on the reflecting surface, was found to be due to interference between the two surfaces of the film. When the reflecting surface of the film is examined with the spectrophotometer without an eyepiece and with the ocular and the collimator slits both very narrow, characteristic interference bands are plainly seen. These bands move across the field of view, when the film is shifted in its own plane toward either a thicker or thinner part. The effect of this interference is eliminated as follows. The telescope objective is diaphragmed by a vertical slit 1.5 mm. wide, approximately wide enough to show one light interference band or one dark band at a time, at the ocular slit. Then the reflection is measured for one wave-length, at one point on the film. The film is next moved in its own plane a very small distance, as described above, and the reflection again determined. This process is repeated until the maximum and the minimum in the reflection can be determined for any one wave-length. The whole procedure is then repeated for other wave-lengths. The average of these values is given in the results as the true reflection. The films are sufficiently prismatic to change the order of interference by one, for a motion as described above, of .35 mm., determined by calculation from the known variation in thickness of the film, and also by trial. Within

this limit, the true reflection is considered a constant, although it varies considerably in going a distance of 10 mm.

The data obtained from film No. 9 are given in Table IV. and

TABLE IV.

Reflection of cathodic film, No. 9.

Wave-length.	Maximum Reflection.	Minimum Reflection.	True Reflection.
673	.0695	.0530	.0613
650	.0530	.0377	.0454
626	.0604	.0424	.0514
599	.0477	.0361	.0419
576	.0395	.0354	.0375
556	.0351	.0309	.0330
537	.0367	.0314	.0341
518	.0380	.0334	.0357
502	.0370	.0346	.0358
490	.0333	.0299	.0316

represented graphically in Fig. 8. Aschkinass [1] gives the reflection of polished gas carbon as 4.4 per cent. at the *D* line, increasing to nearly 100 per cent. for Hertzian waves. The reflection of a cathodic carbon surface, at the *D* line, is seen from the curve to be 4 per cent. There is apparently a very slight rise in the reflection

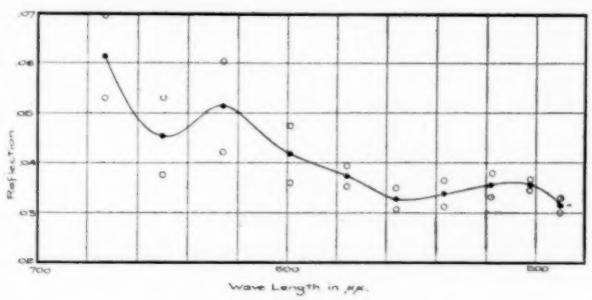

Fig. 8.

curve of cathodic films at 630 $\mu\mu$, corresponding closely to the slight anomaly as shown in curve *A*, Fig. 9. If there is a corresponding variation in the transmission, it is very slight. Nichols and Blaker [2] found a maximum in the rate of increase of radiation

[1] Aschkinass, Ann. d. Physik, IV., Vol. 18, p. 373, 1905.

[2] Nichols, PHYS. REV., Vol. 13, p. 129, 1901; and Blaker, l. c.

with temperature, using carbon rods and filaments, between the wave-lengths 620 $\mu\mu$ and 700 $\mu\mu$, the exact position varying with the temperature. The reflection of the incandescent lamp films was not obtained, because of their curvature. The refractive index curve

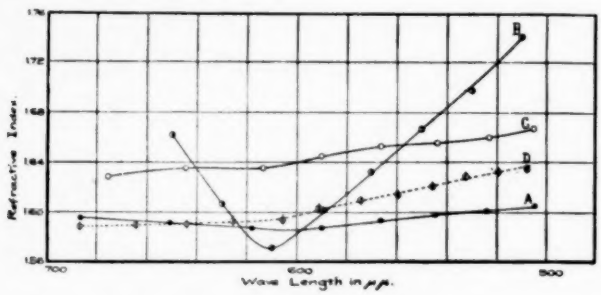

Fig. 9.

for these films, as well as the anomaly found by Wood[1] in similar films deposited on plate glass inside an incandescent lamp globe, suggests the probability of an abrupt change in their reflection.

REFRACTIVE INDEX OF CATHODIC FILMS.

To obtain the refractive index of a film by interference methods, it is simply necessary to determine the "air thickness" and the "optical thickness" at the same point, in terms of the wave-length considered. The ratio of the latter to the former gives the index.

To determine the air thickness, the carbon film is cleaned away from a portion of the glass plate and another plate is put over it, forming a layer of air between the plates on one hand and the front plate and the film on the other. Then if light reflected from these surfaces is resolved by a prism or a grating, two sets of "spectral air bands" will be seen, as when the spectrometer with two collimators is used: one, due to interference between the two inner glass surfaces; the other, to interference between the free carbon surface and the glass surface over it. If these surfaces are slightly inclined to each other, in such a way that the "spectral bands" are parallel to the collimator slit, and are approximately plane, the "air thickness" of the carbon film at any point is readily found by a formula

[1] Wood, l. c.

due to Dr. Brace ;[1] or, by a slightly simpler formula, as follows. Let n_1 be the number of "spectral bands" between two definite points in the spectrum, arising from interference between the glass surfaces ; let n_2 be the corresponding number, after the reflecting plates have been moved a certain distance in their own plane ; while m represents the number of "spectral bands" that have moved past any wave-length, λ, during this shift. Further, let N_1 be the "order of interference" — twice the distance between the two reflecting surfaces at the initial position — measured in terms of λ. Then

$$N_1 = \frac{n_1 m}{n_2 - n_1}.$$

m is + or −, according as the shift of "spectral bands" is toward the red or toward the blue. Let N_2 be the corresponding "order of interference" between the glass and the carbon surfaces at the same point. Then N, the "air thickness," follows directly :

$$N = \frac{N_1 - N_2}{2}.$$

The cathodic films are highly transparent to the longer wave-lengths ; hence, the assumption was made that there is the same change of phase on reflection from carbon as from glass, for these wave-lengths. (There is no evidence of a sudden change of phase, such as Cartmel[2] noticed in the case of fuchsin.) This assumption is the same as was made by Pflüger[3] in the case of reflection of red light from fuchsin, which is many times more opaque than carbon, even for those wave-lengths for which the former is most transparent. Since this assumption requires the choice of dark bands[4] for measurements, these were made in every case by setting upon the dark, rather than upon the light, bands.

To obtain the "optical thickness," two methods were used. The first, or "spectrometer method," is identical in principle with the

[1] Brace, Phil. Mag., V., Vol. 48, p. 350, 1899 ; also Rendtorff, Phil. Mag., VI., Vol. 1, p. 359, 1901 ; and Williams, PHYS. REV., Vol. 18, p. 280, 1904.

[2] Cartmel, l. c., p. 222.

[3] Pflüger, Wied. Ann., Vol. 65, p. 203, 1898.

[4] Brace, PHYS. REV., Vol. 21, p. 291, 1901.

method just described above, for the "air thickness." The upper glass plate is removed, and interference takes place between the two surfaces of the film, giving "carbon bands" in the spectrum, from which M, the "optical thickness," is obtained. The refractive index, μ, for the wave-length λ, is the ratio of M to N, as above. If $\lambda_1, \lambda_2, \cdots, \lambda_k$ are the wave-lengths, from λ toward the blue, corresponding to the centers of the successive "carbon bands," the refractive index for each of these wave-lengths is

$$\mu_k = \frac{(M+k)\lambda_k}{M\lambda}\mu ,$$

where M is the "optical thickness," in terms of λ. Table V. gives the refractive index obtained by this method, for cathodic film No. 7, which gave an especially distinct set of "spectral bands." These results are represented by curve A, Fig. 9. Film No. 9 gave a similar curve, though about 3 per cent. higher in the red, rising to 4 per cent. in the blue. (See Table VI., and curve C, Fig. 9.) Film No. 9 was more highly absorbing than No. 7 for the same thickness; hence was probably denser.

TABLE V.

Refractive Index of cathodic film, No. 7; *spectrometer meth d.*

Order, *M.*	Wave-length.	Refractive Index.	Order, *M.*	Wave-length.	Refractive Index.
19	687	1.596	24	545	1.599
20	651	1.592	25	524	1.601
21	618	1.588	26	505	1.605
22	590	1.588	27	487	1.609
23	567	1.594	28	472	1.617

TABLE VI.

Refractive index of cathodic film, No 9; *spectrometer method.*

Order, *M.*	Wave-length.	Refractive Index.	Order, *M.*	Wave-length.	Refractive Index.
19	676	1.629	23	566	1.653
20	646	1.636	24	544	1.656
21	614	1.636	25	523	1.660
22	589	1.645	26	505	1.667

This method is very advantageous, where the films are prismatic and are neither too thick nor too thin to give good bands; because the retardation of one interfering ray over the other takes place entirely in one medium.

The second, or "interferometer method," of obtaining the "optical thickness," in which the interferometer previously described was used, can be used with much thicker films than can the "spectrometer method"; for light traverses the film, which is strongly absorbing, only once in this type of interferometer. It can also be used for much thinner films — films too thin to give "spectral bands" —; for "spectral bands" may be introduced by adjusting the interferometer. As previously described, the instrument is first so adjusted that the retardation in one interferometer path over that in the other is due to carbon, or to air, or to both, and to nothing else. The carbon film, n, Fig. 4, is traversed by the lower half of the beam of light in one path; the rotating part of the mica compensator, k', is in the upper part of the same beam. Two sets of spectral bands appear in the spectroscope, h, one above the other; as when the spectrometer with two collimators is used. The retardation due to the carbon, in terms of the number of "spectral bands" shifted past any one wave-length, λ, is measured roughly by slowly pushing along the glass plate carrying the carbon film, from a point where the retardation due to the carbon is zero. The compensator is then turned until the retardation due to the mica is the same at λ, at the center of a dark band, as that due to the carbon. The process is repeated for other wave-lengths.

The refractive index for any wave-length is

$$\mu = \frac{N + r}{N},$$

where N is the "air thickness" and r, the retardation, both measured in terms of λ. The refractive index of the cathodic films as determined by this method, agrees well with that found by the other method, except in the green and the blue, where the absorption is so great that the spectrometer method is not very accurate. Table VII. and curve D, Fig. 9, show the index of film No. 7, obtained by this method. (Compare Table V. and curve A.) When the inter-

TABLE VII.

Refractive index of cathodic film, No. 7; interferometer method.

Wave-length.	Retardation, r.	Refractive Index.	Wave-length.	Retardation, r.	Refractive Index.
687	3.49	1.589	576	4.32	1.610
665	3.61	1.590	560	4.46	1.614
645	3.73	1.591	546	4.63	1.621
626	3.86	1.594	533	4.80	1.629
605	4.00	1.595	520	4.95	1.633
591	4.15	1.603	508	5.09	1.635

ferometer is used, the method of mixed bands[1] should be applied. However, with the order of thickness used in this work, the error due to neglecting this correction is very small, since the mixed bands include air and carbon bands only.

REFRACTIVE INDEX OF INCANDESCENT LAMP FILMS.

The incandescent lamp films were but very slightly, if at all, prismatic and were on curved surfaces; consequently, the methods of measurement used in determining the refractive index of cathodic films, need some modifications. Obviously, the spectrometer method could not be used; hence, the interferometer method was employed. A lamp was broken into bits, and a piece selected that gave approximately straight "spectral bands" when placed in the interferometer, the light being resolved by a spectrometer with a very short, narrow narrow slit. The incandescent lamp films not being sufficiently prismatic, the order of retardation could not be obtained roughly, as it was for the cathodic films. Instead, the interferometer is set for the central white band in one half of the field, as seen in the spectrometer; then, one of the interferometer plates is moved until the same condition is obtained in the other half of the field, and the consequent shift of bands past any wave-length is counted. This shift, for lamp films, was always less than one band. The exact retardation was determined from the mica-compensator readings as follows. The compensator was carefully calibrated throughout the spectrum, for a shift of each whole band from 1 to 5. The retardation caused by rotating the compensator is

[1] Brace, PHYS. REV., Vol. 21, p. 294, 1905.

$$r = \frac{t(\mu - 1)}{\lambda}\left(\frac{1}{\cos\theta} - 1\right),$$

where t is the "air thickness" of the mica; θ, the angle through which the compensator is turned for the wave-length, λ; and μ, the refractive index of the mica in the direction of the ray. μ is constant for values of θ from 0° to 20°, corresponding to values of r from 0 to 5, as can be shown by plotting values of r and $(1/\cos\theta - 1)$. This makes

$$r = K\left(\frac{1}{\cos\theta} - 1\right),$$

in which K is calculated from the observed values of r and θ within the limits just given. From this equation, calibration curves were calculated and plotted for values of $r = 0, 0.05, 0.1, 0.2, \cdots, 1.0$, since r was always less than unity in practice. The actual retardation caused by the lamp films was then obtained by interpolation from these curves.

To determine the "air thickness" of lamp films, Newton's rings were used. Upon the film side of the bit of glass selected above — from a part of which the film had been cleaned away — was placed another selected piece of the same globe, carefully cleaned all over, and the whole illuminated with strong sodium light. This arrangement gave two sets of Newton's rings, shifted past one another slightly, just as were the "spectral bands" above. This shift was measured for light at nearly perpendicular incidence, by means of a low-power micrometer microscope; and from it, the "air thickness" of the film was calculated. There was a little uncertainty at first, whether the shift of the sodium bands was a part of a band only, or a certain number plus that part of a band. This is settled definitely, however, by the fact that, if the shift is assumed to be a part only of a band, the index becomes 1.602; while, if the shift is assumed to be one whole band plus that fraction, the resulting index is only 1.3, — an improbable value. The "air thickness" of incandescent lamp film No. 15 is thus determined to be .402 wave-length, at the D line. μ_D is then determined from the equation given above,

$$\mu = \frac{N + r}{N}.$$

The refractive index for other wave-lengths is obtained from the equation,

$$\mu_x = 1 + \frac{r_x \lambda_x}{N_D \lambda_D}.$$

The results from the above film No. 15, are shown in Table VIII. and are represented by curve *B* of Fig. 9.

TABLE VIII.

Refractive index of incandescent lamp film, No. 15 ; *interferometer method.*

Wave-length.	Retardation, r.	Refractive Index.	Wave-length.	Retardation, r.	Refractive Index.
650	.241	1.662	570	.263	1.633
630	.228	1.607	550	.287	1.667
610	.222	1.572	530	.312	1.698
589	.242	1.602	510	.344	1.741

The refractive index of every film examined shows anomalous dispersion, although it is very slight in all of the cathodic films. In these, the anomaly probably corresponds to a "point of inflection"[1] in the refractive index curve. There is a corresponding variation in the reflection of cathodic films, but little or no evidence of a variation in the absorption, even in the case of incandescent lamp films, in which the anomaly is most prominent. The lamp films examined were somewhat thicker and more porous than is usual with such films. Wood's films[2] were deposited on plate glass inside a lamp globe ; hence the deposit was formed at a place much nearer the incandescent filament than in the case of mine. His were, in consequence, probably much denser than mine. This would account for his higher value of the refractive index, 2.2 for the *D* line, as compared with my value of 1.6.[3] Amorphous carbon absorbs nitrogen so strongly that it probably is really a solution of nitrogen and carbon, as Stark[4] suggests for smoke films.

[1] Brace, PHYS. REV., Vol. 21, p. 293, 1905.

[2] Wood, l. c.

[3] Professor F. Braun, of Strassburg, has kindly sent me a number of carbon films made by "flashing" a filament near a glass surface. He has shown (Ann. d. Physik, IV., Vol. 17, p. 359) that these films are deposited directly from the vaporous condition. Consequently, they are much denser than those I have thus far examined. I hope to be able to determine the optical properties of these later.

[4] Stark, l. c.

Its properties, therefore, are those of a solution, and not of pure carbon.

Different samples examined thus far vary so much, that it appears conclusive that the optical properties of carbon films, and probably of other substances as well, are not constant ; but are complex functions of the conditions and methods of deposit. This is to be expected from the work of Kundt,[1] Hagen and Rubens,[2] Stone,[3] Longden,[4] Patterson,[5] Beilby,[6] and others, upon both the optical and the electrical properties of thin films of metals. The suggestion of Kundt and of Hagen and Rubens, that this variation for certain metals may be due to the formation of oxides, is not so satisfactory in the case of carbon, since its oxides are gases.

Recapitulation.

1. The reflection, the absorption, and the refractive index of carbon films vary with the conditions and method of deposit.

2. There is a slight anomaly in the refractive index of cathodic carbon films, and a more pronounced one in the case of incandescent lamp films, at the wave-length $\lambda = 610\ \mu\mu$. The reflection curves of the former show a corresponding variation. Scarcely any variation, however, has been detected in the transmission curves of either class of films.

3. The transmission of cathodic films decreases almost uniformly from the red of the visible spectrum to the wave-length $\lambda = 226.6\ \mu\mu$, beyond which the films are completely opaque. Thus there is no pronounced absorption band.

4. The reflection of cathodic films *decreases* from a maximum in the red to a minimum in the blue of the visible spectrum. A slight rise, however, occurs at the wave-length $\lambda = 630\ \mu\mu$.

In conclusion, I wish to express my grateful appreciation of the assistance and inspiration given me in this work by the late Dr. D. B. Brace, and also of the excellent laboratory facilities placed at my disposal in the University of Nebraska, where it was done.

Syracuse University, June, 1906.

[1] Kundt, Phil. Mag. V., Vol. 26, p. 1, 1888.
[2] Hagen and Rubens, Phil. Mag., VI., Vol. 7, p. 164, 1904.
[3] Stone, Phys. Rev., Vol. 6, p. 1, 1898.
[4] Longden, l. c.
[5] Patterson, Phil. Mag., VI., Vol. 4, p. 652, 1902.
[6] Beilby, Proc. Roy. Soc., Vol. 72, p. 226, 1903.

THE MOISTURE PRECIPITATED IN THE FOG CHAMBER PER CUBIC CENTIMETER.

BY CARL BARUS.

1. Elsewhere[1] I have shown that the combination of fog chamber with a large vacuum chamber and a sufficiently wide passageway, though affording superior practical advantages, and little if any inferiority in efficiency to the piston apparatus within the range of measurable coronas, nevertheless does not show the volume expansion of the air within the fog chamber either under adiabatic or under isothermal conditions. It makes no difference how rapidly the stop cock is manually closed, the conditions of the vacuum chamber are always impressed upon the fog chamber. The adiabatic and isothermal data may, however, be computed, if the volume ratio of the fog and vacuum chambers and the pressures before exhaustion (when the chambers are isothermally separated) and after exhaustion (when the chambers are isothermally in communication) are known; and these computations are simple because the reductions are practically linear.

When the vacuum chamber is large, moreover its pressures vary but slightly, and therefore the pressure observed at the vacuum chamber after exhaustion, when the two chambers are in communication, is very nearly the adiabatic pressure of the fog chamber. This result makes it easy to compute the water precipitated per cubic centimeter, without stopping to compute the other pressures, with a degree of accuracy more than sufficient when the other measurements depend on the size of coronas.

2. To show this, let d, L, and π refer to the density, latent heat of evaporization and pressure of water (or other) vapor; let ρ, k, c, t, denote the density, specific heat at constant pressure, specific heat at constant volume and absolute temperature of the air, the water vapor contained being disregarded apart from the occurrence of condensation. Let the variables, if primed, belong to the vacuum

[1] American Journal of Science.

chamber otherwise to the fog chamber. When used without subscripts, let them refer to isothermal conditions or to room temperature. Let the subscript 1 refer to the adiabatic conditions on exhaustion; the subscript 2 to isothermal conditions, if the chambers could be isolated immediately after exhaustion and allowed to heat and cool from the adiabatic state independently. This case is actually realized in the piston apparatus. Let the subscript 3, finally, refer to the isothermal conditions which prevail if the chambers are put in communication at a room temperature after exhaustion. Then the usual equations for the heat evolved in the condensation of vapor, leads easily to

$$\bar{d} = [d_1] - \rho_2 c(\bar{t} - t_1)/L \tag{1}$$

where $\bar{d}$ is the density of saturated vapor at $\bar{t}$, if $\bar{t}$ is the temperature to which the wet air is heated from its adiabatic temperature t_1, in consequence of the condensation of water vapor, and where $[d_1]$ is the density of water vapor if cooled as a gas (*i. e.*, without condensation) from t to t_1. Moreover,

$$[d_1] - \bar{d} = m, \tag{2}$$

the mass of water precipitated per cubic centimeter by condensation, or the quantity sought.

If Boyle's law is assumed to hold both for the gaseous water vapor, $[d_1]$, and for the wet air, it is convenient to reduce equation (1) to room temperature (isothermal state), and it becomes

$$\bar{d} = d\frac{p_2 - \pi}{p - \pi} - \frac{\rho c}{L}\frac{p_2 - \pi}{p - \pi}\left(\bar{t} - t_1\right). \tag{3}$$

If the vapor density of saturated water vapor is known at a temperature as low as $\bar{t}$,

$$\bar{d} = f(\bar{t}) \tag{4}$$

so that $\bar{t}$ (the only unknown quantity in equation (3), since the equation of adiabatic expansion determines t_1) is found from the intersection of the curves (3) and (4). This is the method of Wilson[1] and of Thomson.

[1] C. T. R. Wilson, Phil. Trans., London, Vol. 189, p. 298, 1897.

3. In the piston apparatus p_2 as well as p may be read off at the gauges: but as stated above, this is not true when the fog chamber communicates directly with the vacuum chamber. In this case, however, p_1 is nearly given by p_3. Consequently it is expedient to reduce equation (1) to the adiabatic conditions, whence

$$\bar{d} = d\left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k} - \frac{\rho c}{L}\left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k}(\bar{t} - t_1) \tag{5}$$

$$\tau_1 = \tau\left(\frac{p_1 - \pi_1}{p - \pi}\right)^{(k-c)/k} \tag{6}$$

$$m = \frac{\rho c}{L}\left(\frac{p_1 - \pi_1}{p - \pi}\right)^{c/k}(\bar{t} - t_1) \tag{7}$$

Here π_1, the vapor pressure at t_1, is usually negligible (about .5 cm.) as compared with p_1, and p_1 may in practice (where great accuracy is not demanded) be replaced by p_3, which like p is read off, while π holds at t, which is also read off.

4. In conclusion I will give a numerical example taken from a preceding paper, (l. c.) where

Observed.	Computed.
$p = 76$ cm.	$p_1 = 46.1$ cm.
$\pi = 1.7$ cm.	$p_2 = 54\,7$ cm.
$\rho = .00118$.	$t_1 = -17.8°$ C.
$p' = 43.5$ cm.	$\bar{t} = +5.25°$ C.
$p_3 = 45.5$ cm.	$t_1' = 24.1°$ C.

If equation (3) is taken,

$$m = 5.36 \times 10^{-6} \text{ grams per cm.}^3$$

If equation (5) is taken,

$$m = 5.35 \times 10^{-6}.$$

If equation (5) is taken and p_1 replaced by p_3,

$$m = 5.30 \times 10^{-6},$$

the error being 1 per cent. of the true value, which is quite near enough in practice and admits of easy correction.

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ON INCREASING THE CONSTANCY OF BATTERIES GIVING CURRENTS.

By W. P. White.

IF a storage battery while charging is also made to give a current nearly equal to the charging current, very little electricity will flow through the battery, whose action is then to steady the voltage of the current source. The idea is familiar of using an accumulator battery in this way where storage of energy is a secondary consideration. An application of the same principle renders it possible, with an arrangement of primary or secondary batteries alone, to obtain current at a steadier voltage than would be possible with the same number of cells connected parallel. The arrangement is simple enough in theory: it may, however, deserve a brief description.

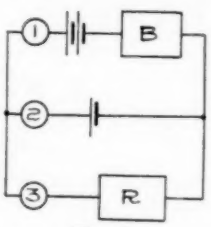

Fig. 1

The disposition of the cells is shown in the figure. Branch (1) contains a battery and a resistance box. The voltage in this branch is V and the resistance B. Branch (2) contains another battery of smaller voltage, v, and of resistance, b. Branch (3) contains the apparatus through which it is desired to send constant current or current at constant voltage. Its resistance is R. By proper adjustment of the resistance, B, it is possible to make the current through branch (2) as small as we please, and therefore to keep the battery in that branch constant. At the same time the value of the current through (3) can be made to depend largely or entirely upon the constant battery (2), and only slightly, or not at all, upon the battery in (1), which sends the current. The current through (2), I_2, is,

$$\frac{VR - v(B + R)}{BR + b(B + R)}. \qquad \text{(I.)}$$

The condition for this to be zero is evidently

$$\frac{V}{v} = \frac{B + \mathrm{R}}{R}. \qquad \text{(II.)}$$

If $V = 2 \times v$, $B = R$. In this case, adjustment is particularly easy since any change in R can be approximately compensated by making the same

change in B. Moreover, this arrangement can be secured with the smallest possible number of cells, three. In what follows, it will be sufficient to discuss this particular case. If V varies — as it must be supposed to do, otherwise there would be no object in using more than one cell — or if the adjustment of B is not exact, the effect on the voltage of the battery in (2) will be small. For instance, if the current I_1 flowing through (1) causes a variation of 1 per cent. in V, the resulting current in (2) will be 2 per cent. of I_1, and should cause a variation in v of less than .02 per cent.— usually much less. If the variation in V is 10 per cent., the variation in v may be as much as 2 per cent., in which case this arrangement is little better than the three cells in parallel.

The current which it is desired to regulate, I_3, equals

$$\frac{v + V\frac{b}{B}}{R + (R + B)\frac{b}{B}}. \qquad \text{(III.)}$$

This equals v/R as long as the condition (II.) holds, regardless of the resistance in (2) or of any variation of V.

Hence by putting an ammeter in the branch (2) and adjusting B so that I_2 remains approximately zero, I_3 can be kept as close to v/R as desired — a somewhat troublesome arrangement, but one which might prove of value if it were necessary to get constant results with rather poor batteries. If V or the adjustment of B varies, I_3 will vary; that is, the conditions which cause a currrent through branch (2), and thereby may cause a variation in v will also for another reason cause a variation in I_3, whether v varies or not. This second variation is nearly proportional to b/B and may be made very small. The arrangement of cells here described, therefore, works best with batteries of low resistance. It is also better adapted for increasing greatly the constancy of a battery already fairly constant than for improving a poor one. It is especially effective with storage cells, to which the writer has applied it. In particular, it is well suited to give constancy in the main current of potentiometers of very low resistance where storage cells of the usual capacity generally show troublesome fluctuations.

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